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

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Lecture 14

In the last lecture I described the in-situ polymerization analysis using diffusing spectroscopy analysis and also I have shown you that how simple geometry based calculations can be used to find out the tortuous path which is traversed during that ink infiltration into the binder jet, during the binder jet printing into the powder bed. Taking one step forward, I will be showing you that what is the time scale of the binder powder interactions. Again we go back to the basic description of the avalanche of the binder droplets from the printer head and this binder droplet essentially will be traversing into the powder bed and this powder bed thickness is 80 to 100 micron. And if you see that what is the characteristic time t* is nothing but t X by V by d_0 where V is equal to velocity of droplet and it is 2.5 m/s and average droplet diameter is 8.5 μs and minimum residence time is 8.

6 s What you see that you know modified powder bed thickness that is based on our calculations let us say 80 to 100 micron and what you now can perceive that is when the binder infiltrates this initiator, accelerator and monomer they interact and they trigger the in-situ polymerization reactions which form this kind of polymeric chains. And these polymeric chains essentially will hold the powder materials rather strongly and it is more like a physical interactions and physically these polymer chains will hold the powder very strongly and that actually helps in the overall binding of the powder bed. Now, from the simple calculations of the t* is equal t X V by d_0, one can find out that typical t* values if it is 1.8 μs, it is more like initial impact.

When time scale changes to more like 0.18 to 1.8 milliseconds, it is more capillary driven spreading. If it is more than 1.8 milliseconds to 8.

6 seconds, it is equilibrium attainment. These are like some of the very basic description as how binder powder interactions takes place in real time. This is what I have already described to you, but what is the second point? First point is well taken. Second point is that if you add 2 gram of the initiator APS in 100 gram Ti6Al4V powder, then molarity of the initiator is like 0.

54 M. The propagation rate constant during the in-situ polymerization of acrylamide addition polymerization is K inverse is 130 seconds. The time scale of polymerization is order of magnitude higher than the equilibrium residence time and therefore, would extend to a large number of layers and thereby trap the powder particles. What it essentially means is that what is the time scale of the acrylamide polymerization? This is the in situ polymerization, right. What is the inferences that one can draw from this simple mathematical calculations? Because these mathematical calculations are important because those are used to validate some of the process science that we have discussed earlier. What I am trying to show you is that during this in-situ polymerization, this polymerization We wanted to know that when this APS initiator interacts with the accelerator and in the monomeric solution, when it will trigger the acrylamide addition polymerization, what is the time scale that this polymerization takes place.

And from this what is found out it is 130 seconds and this 130 seconds is much higher than equilibrium residence time. And what is the equilibrium residence time? It is of the order of few milliseconds. What it means that this infiltration or this polymerization will not be restricted only to 2 layers. but will extend to multiple such layers. And this more the number of layers that this polymerization will be extended, more will be the ability of the ink to infiltrate and also to bind the powder particles.

The efficacy of the binder infiltration, efficacy of the binding or the binding efficacy of the in situ polymerizable ink will be more and more. If this binding takes place or if the addition polymerization extends to much higher time so that it is able to extend to more layers. We will come back to overall time scale of the in-situ time scale of binder infiltration in the powder bed. It is a kind of a summary slide and as I have mentioned to you this is based on the Washburn model which is published in 1921 and this is a very long equations what we are interested in this time scale of binder infiltration. All other physical parameters has been mentioned in this slide.

What you see it is avalanche of the binder particles, binder droplets which will come which will essentially infiltrate into the powder bed and this capillary channel what is you can see in the blue ink region, this is what this binder infiltrates and we can purely go through the simple geometric considerations you can connect these 3 spheres. and you make an equilateral triangle and then you can find out that what is the different radius and this different radius, different length scale and there you can find out that what is the time scale of infiltration. How to rationalize the in-situ polymerization? Suppose if you have n number of powder layers. Therefore, this hour glass shaped capillary elements are (2n-1) having the unit length of 2p. This one is a 2n and one is a 2p and if you look at this what is the total vertical capillary length of the n^{th} layer of powder particle bed is 2p (2n-1).

And, for the analysis of figures a and b, this is the figure number I am referring to that now we are essentially extending our analysis not to 2 layers but to n^{th} layer. Then, we can find out that effective diameter of the capillary is 4n divided by (4n-1) into p. As n increases effective radius reduces which goes well in line with the practical or whatever we have seen in practice. If you consider θ is equal to 0 degree contract angle which is not common which is more for reference in hexane and ϵ is equal to 0. The time required for droplets having diameter 45 μm which we have measured using the shadowgraphy technique to infiltrate into a porous bed of having nearly 4 layers of particle is 77.

5 seconds. This is 77.5 seconds in earlier analysis we have found out the acrylamide addition polymerization rate constant is 130 seconds. Essentially what we are getting 77.5 seconds is much lowest than that of the polymerization reaction constant 130 seconds. Since the time of penetration of the binder fluid into porous powder base should be smaller than the size time of the in-situ polymerization, this will allow binder fluid components to react with initiator mixed with the powder.

This simple calculations essentially validates our theory of in-situ polymerization as well as binder efficacy. Once this 3D printing is over, we have used high temperature heat treatment and then thereafter we have used microcomputed tomography analysis which was introduced to you earlier in one of the earlier lectures to find out what is the 3D microstructure that develops and also to do quantitative analysis. This is the as printed microstructure without any post binder jet printing and we are getting volume fraction of porosity is 52 or 52% volume fraction porosity and shy is 99.8% that is the interconnectivity is 99.

8%. When you do sintering and then after the assintered microstructure you analyze that volume fraction porosity is 28% and integrated porosity is 98.4%. The message that I am trying to send across that post binder jet printing heat treatment reduces the porosity to a significant extent without causing much changes in the pore interconnectivity which is hardly reduced from 99.

8 to 98.4. And this is the number of pores. You can see this pore size, so if you do this kind of distribution you will see this is large tail on the right-handed tail and this pore diameter is somewhere around kind of you know 10 to 12 micrometer. Now if you see that number of pores here you can see that this is also large long tail And here again this pore diameter is almost of the same range but the tail part is much more extended and also there is a clear difference in the particle size distribution. Since the x-axis scale is same, it is not the same, it is difficult to compare these two kind of size distribution. And this table essentially shows you for the number average pore diameter is one case is

around 9 micrometer and in as sintered case like after heat treatment after the 3D printing after the heat treatment it is 12.

5 micrometer. Now, we have measured the strength of this 3D printed structures but the strength measurement was followed by strength reliability analysis. Now what happens in the 3D printed structure, as I mentioned in some of the earlier lecture it contains microporosity and also pores typically generated due to insufficient binder material interactions. And these pores, what is these pores? You have seen these pores kind of 10 to 12 micron. Now these pores are essentially when you do this 3-point bend test for example or 4-point bend test so these pores are essentially distributed in the structure right in a random manner. larger the pores more is the stress concentration so because it acts as a defect.

larger the pores more is the defect size and that can essentially cause the failure of the materials. depending on whether there is a porosity variation , if you consider this particular rectangular bar specimen contains that capital N number of small volume elements, you can consider this as a you know rectangular cross section samples. these porosity are randomly distributed . The volume element Containing larger pores will fail fast leading to failure of entire samples.

right. this actually leads to a theory called weakest link fracture statistics. as I have mentioned earlier in previous lecture that it is not a material science course so I cannot cover all the elements of the material science particularly on the mechanics aspect and microstructure aspect. But every now and then whenever it is required, I will explain to you in the simplest possible manner so that you are able to follow and appreciate what I am trying to make you understand. this weakest link fracture statistics is more relevant for porous materials or for materials with defects. Because the moment a material has defects, how these defects are distributed in the materials that one cannot predict a priori or that one cannot assume that how whether defects are uniformly distributed and that is the most ideal case, but in most realistic cases defects are always randomly distributed in the materials.

the microscopic region what I am showing you this microscopic region containing the critical defect size. Critical means in terms of sizes or in terms of the favorable orientation with respect to the loads that particular microstructure element experiences under actual loading conditions. that those volume elements are most likely to fail fast and if that microstructure element fails fast that will lead to the failure of the entire sample. And that was the basic assumption or basic hypothesis on which weakest link fracture statistics was built and then person who has essentially first proposed a scientist named Weibull and that is why it is known as the Weibull's theory. this is in a sense this

weakest link fracture statistics and in the weakest link fracture statistics essentially is based on the probability theory.

The probability theory is that survival probability of any volume element is equal to 1 minus failure probability. or failure probability of one volume element is essentially 1 minus survival probability. if this probability, if the total sample comprises of 'N' number of volume elements, each will have its distinct probability of failure. And when you do this complete failure probability of the total volume elements then you can essentially put it as n number of volume elements and then you can essentially find out that what is the failure probability and if you do this failure probability calculations, this probability of failure as a function of fracture strength for this kind of 3D printed materials and after the post-processed like sintered, 3D printed and sintered Ti6Al4V, we have taken 18 samples. larger the number of samples that you test under the 3-point bending.

this is essentially used in the flexural loading conditions more is the good statistics. essentially if you plot this probability of failure of fracture strength it shows this kind of similar kind of graph. But if you take ln[ln(1/(1-Pf)] where Pf is the failure probability if you plot as a function of the fracture strength. you get almost like a linear variation, the slope of this linear variation will give you the Weibull constant 8.

06 ~ 8.1 and then sigma this is a characteristic strength value you get around 98.5 megapascal. just to show you this kind of materials has a Weibull modulus of 8.1. which is very close to that of the many brittle ceramics because many of the brittle ceramics like alumina their viable modulus is very low.

like 3 or 4 if it goes to zirconia and all it can improve but viable modulus for many ceramics is not above 10. when the Ti6Al4V is metal but it contains porosity and sufficient porosity if you remember that these particular materials as a volume fraction of porosity around 0.28. volume fraction , means 28% porosity if the Weibull modulus is 8.1 that is quite good, quite acceptable in this particular case.

And this Ti6AL4V binder jet 3D printed in-situ polymerized using in-situ polymerized binder. Their compressive strength is more than 200 megapascal and also modulus is 4 gigapascal and Vickers hardness is 6.2 gigapascal. And one of the things that we have done is that trying to find out that how the surface properties also change because the surface roughness and surface properties are important because that will govern the cell-material interactions. And here in commercial Ti6Al4V our surface roughness is 0.

1 micron and whereas the SLM printed is 11.9 micron whereas 3D inkjet printed materials we get is like 8.5 micron. And, contact angle if you see in the SLM printed it is

around 60 degree whereas in case of 3D printed and inkjet printed it is more towards the hydrophobic side it is like 85 degree whereas in commercial Ti6Al4V, commercial essentially means this is the metallurgically processed like conventionally processed. Metallurgically processed means this is like you know this is like either forced or rolled Ti6Al4V and then what we get is like R_a value is 0.

1 micron and contract angle is 51 degree. we have done some cytocompatibility analysis or cell compatibility analysis of these materials. We have used the fibroblasts that is connective tissue cells or osteoblasts that is the bone forming cells. And this particular cell compatibility study was important because we are concerned about the use of specific binder and we have to be absolutely sure the use of binder and if that actually remain there or if any residual binder in the 3D binder jet printed structure should not cause any negative impact on the cell viability. And what we have found out that MC3T3 osteoblast cells are able to grow in a very linear manner from day 3 to day 7. DNA content also increases at these 4 different materials.

One is the control, this black box is the control. This is the commercial that is metallurgically processed. essentially the commercial SLM, this is SLM selected laser melted and this is the 3D binder jet printed structures. This is for the osteoblast cells and this is for the fibroblast cells and you can see 3D inkjet powder printed structure has similar or even statistically higher number of cells compared to the control or metallurgically or the commercial samples. Now when we have stained this fluorescent intact and then we have used that fluorescence microscopy to image the cells which are adhering on the structure, this 3T3 fibroblast cells if you see on the 3D printed structures it very well spread.

The same is true for the 3D inkjet printed structures for these materials when we have done this osteoblast cells and this is the actin stained and you can see MC3T3 that is osteoblast cells which are adhering on these materials. And when you do this fluorescence microscopy, if you see this blue stained regions, these are like nucleus of the cells. And other color features what you see apart from blue stain region, these are like cytoskeleton. what you can see clearly when the cells will adhere on this material surface, there is clear cytoskeletal reorganization that has taken place and which leads to good binding on that good cell adhesion and proliferation on these materials. this is that overview of what I have covered in last two lectures on the 3D binderjet printing of Ti6Al4V and you can clearly see that I have shown you couple of features, one is the 3D microstructures, this is the 3D binderjet printed.

And, followed by sintering that leads to strength reliability of 8.1, it has volume percent porosities 28% and it also supports cyto compatibility without any compromise. this

paper was published in Biomaterials in the year 2019 and you can see more details if you would like to follow this particular paper. And with this I close the scientific case study on binder jet 3D printing of the Ti6Al4V. Thank you.