Additive Manufacturing of Salt Hydrates: Primary Process Parameters and Case Study

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Abstract. This paper pr esents the l atest out comes in the field of additive manufacturing. Some s alt hydrates as printing materials provide many advantages (such as good a vailability and low toxic behaviour) compared to other materials, thus making them p articularly suitable for s pecific ap plications. A layered d eposition m ethod for s alt hydrates is developed from the binary phase diagram of sodium acetate trihydrate, which is first described mathematically. The experimental results then verify the theoretically described method. Thus, the presented process can also be applied to other salt hydrates which are based on the same physical basic principles. Moreover, this novel process has been termed as Subcooled Liquid Printing (SLP) by the authors.

1 Introduction

The global m arket s ize of additive m anufacturing h as increased significantly in recent years [1], [2]. This is due to the potential of producing complex geometries in a reasonable time at an affordable cost [3], [4]. As a result, the i ndividualization o f p roducts (mass c ustomization) can n ow b e r ealized without t he n eed for considerable additional effort, and the time to market for new products has been significantly reduced [5], [6]. During the past few years, s ome ad ditive m anufacturing t echnologies, such as the FDM, SLM and SLA processes, have even been s uperior o ver co nventional m anufacturing technologies (e.g. mold making). For mold making in the case of highly c omplex ge ometry l ike u ndercuts, t he question of demolding comes into focus. Solvation is one common method f or r emoving t he mold. W ith t his method, the solvation temperatures of both the casted and the mold material are crucial. The molds of salt hydrates are suitable for mineral based casting materials such as concrete d ue to their l ow solvable temperatures. To utilize the advantages of additive manufacturing and salt hydrates i n m old m aking, a new a pproach of additive manufacturing process is developed.

Recent s tudy i ndicates t hat t he o utlining factors t o expand the field of application for additive manufacturing technologies are using new materials and increasing the speed of the processes [7], [8]. Due to the high specific latent heat, salt hydrates are primarily researched as phase change materials in latent heat storage systems. For instance, space h eating a nd d omestic h ot water preparation [9], s olar h eating s ystems [10], and r adiant floor heating systems [11]. A literature review shows that there is no additive manufacturing technology using salt hydrates as printing material. In recent years, only the salt hydrates aqueous sodium chloride and ammonium chloride have been investigated as a novel cold source for the platform [12]. Hence, this paper at tempts to address this l ack of r esearch in u sing s lat hydrates for ad ditive manufacturing processes.

2 Material

In this section, the materials involved in the newly developed ap proach has been described. The chemical composition and s tructure of s alt hy drates and s odium acetate trihydrate has been elaborated. Further references have been given which illu strates their us age in this additive manufacturing process.

2.1 Salt hydrates

A salt hydrate is a crystalline salt molecule that is loosely attached t o a cer tain n umber o f water molecules. T he properties such as solvation temperature and toxicity of a salt hydrate (e.g. sodium acetate trihydrate) depend on the crystalline salt molecule a nd t he number o f a ttached water molecules. Thus, they differ significantly. Sodium acetate tr ihydrate (SAT) is d istinguished mainly b y th e good availability and the low to xic behaviour compared to other salt hydrates [13], [14]. Therefore, handling and processing of SAT is viable without any material-specific safety precautions. Hence, this salt hydrate is examined in this paper in more detail.

2.2 Sodium Acetate Trihydrate (SAT)

The chemical structure of SAT contains three molecules of water whereas, sodium acetate (SA) is the anhydrous form o f S AT and contains n o water molecules. The binary p hase d iagram o f S A and water, as shown in figure 1, provides information on the states o f aggregation at d ifferent t emperatures and aqueous solution concentrations. [9]



Figure 1. Phase diagram of SA and water [9].

As exhibited in this diagram, one area in which the SA a queous solution c an a ssume t wo states of aggregation: the stable s olid s tate and the metastable (subcooled) l iquid s tate (Liquid+SAT) is seen. T his subcooled state of a ggregation can be converted into a stable state of a ggregation by a di sturbance which triggers the crystallization. This property of SA aqueous solution is used for an additive manufacturing process. The binary phase diagram shows that there are two main process parameters in the additive manufacturing process: the temperature T and the concentration w. The following case s tudy investigates the i nfluence of t emperature, concentration, and other essential process parameters on the properties of the deposited layers.

3 Process

In this section, the thorough process of sodium a cetate trihydrate is e laborated. The experimental set-up of the process i sel ucidated which i s followed b yt he classification of g cometry of the deposited l ayer. A mathematical model is then described for the calculation of ideal periodicity length.

3.1 Experimental setting for depositing layers

An ex perimental model was s et-up f or a nalysing a nd testing t he process. It c onsisted of h eating a nd c ooling systems, p umps, t emperature s ensors, a nd a nozzle. Figures 2 and 3 illustrate the experimental setting used to carry out the case study.



Figure 2. Experimental setting using the solidification process of SAT.

First, S AT (crystalline white p owder) a nd w ater (liquid) a re mixed in a v essel (no. 1) a t a mbient temperature (T_1) in a d efined concentration w. U sing a heating system (no. 2) the mixture is heated to T_2 , which is higher than the solvation temperature T_s , and it changes into a liquid state, i.e., a solution. This solution is pumped to the cooling system (no. 4), where heat is removed from the solution to c ool it d own from temperature T_2 to T_3 , which is s till s lightly a bove the solvation temperature. Subsequently, t he s olution i s ej ected as d rops or a j et from a n ozzle o utlet (no. 5). T he t emperature must b e measured throughout the entire process (no. 6, no. 7 and no. 8). The data from these temperature sensors are input into the controller (no. 9), which regulates the flow rate of the pump (no. 3).

Figure 3 describes in detail the crystallization process which occurs after the solution is ejected from the nozzle outlet (step 1). W hile d ropping o nto the p latform (distance h_{nl}) the solution c ools d own and t urns i nto metastable (but still liquid) state (step 2). The metastable solution i mpacts on a p latform (step 3) and crystallizes rapidly (step 4). A solid layer (width w_l and thickness t_l) is deposited. Due to the crystallization, the latent heat is released and t he t emperature o f t he d eposited l ayer increases. This latent heat must ultimately be discharged into the environment (step 5).



Figure 3. Deposition of solid layers of SAT.

3.2 Classification of t he g eometry of the deposited layer

The d eposited l ayer at t he p latform can b e cl assified according t o i ts g eometry into c ontiguous a nd n on-

contiguous as well as uniform and non-uniform, shown in figure 4.





While u niform g eometries (type 1 and 2) y ield a regular a nd repeatable d eposited layer, contiguous geometries (type 1 and 3) ensure bonded layer structures. To de posit bot h r egular a nd bon ded l ayer s tructures, therefore, geometries of type 1a and 1b (layered or dotted structures) are preferable to all other types.

To classify a deposited layer of type 1, the properties layer width w_l , layer p eriodicity le ngth l_l and the layer thickness t_l (illustrated in figure 4) are u sed. These properties depend on the nozzle diameter d_n , the distance between nozzle and the deposited layer h_{nl} , the feed rate v_f and the nozzle outlet velocity v_n . These are shown in detail in figure 5.





As can be seen in the above figure, the layer width is the maximum dimension of a deposited layer, when measured o rthogonally t o the feed d irection. The layer thickness is the dimension in the direction of the nozzle outlet velocity. The layer periodicity length in dicates a t what distance in the feed direction a structure of the layer begins to be repeated. Going forward, in this paper, the layer periodicity length is investigated in more detail.

3.3 Mathematical model for the layer periodicity length

For un iform a nd c ontiguous layer s tructures (type 1 in figure 4) the layer p eriodicity length can b e d erivated theoretically when the droplet is formed at the nozzle via the balance o f f orces. Also, t his d erivation can b e applicable for geometries of type 2.

The static balance of surface force, weight force, and momentum force are the basis for equation (3.1), which describes the volume of the liquid drop V_{drop} separating from the nozzle.

$$V_{drop} = \frac{d_n \pi}{g} \left[\frac{\sigma_s}{\rho_s} - \frac{d_n v_n^2}{4} \right]$$
(3.1)

In this equation, g is the gravity acceleration, σ_s the surface tension of the solution, and ρ_s the density of the solution.

When t he c ontinuous flow r ate of t he solution generated b y t he p ump i s co rrelated w ith t he d iscrete liquid drops s eparating f rom t he n ozzle, t he l ayer periodicity l ength, ex pressed i n eq uation (3.2), can b e derived.

$$l_l = \frac{V_{drop} v_f 4}{v_n d_n^2 \pi} \tag{3.2}$$

When combining e quations (3.1) and (3.2), equation (3.3) is formed.

$$l_l = \frac{v_f}{v_n g} \left[\frac{4 \sigma_s}{d_n \rho_s} - v_n^2 \right]$$
(3.3)

Since v_n has a considerably lower dimension than the first te rm, it can b e n egated. H ence, (3.3) can b e simplified as shown in equation (3.4).

$$l_l = \frac{v_f}{v_n g} \frac{4 \sigma_s}{d_n \rho_s} \tag{3.4}$$

In equation (3.4), the density and the surface tension of t he s alt hy drate s olution de pend s trongly of t he concentration and the temperature [15], [16].

Furthermore, for the dimensionless speed ratio of feed rate $v_{\rm f}$ and the nozzle outlet velocity $v_{\rm n}$, the given name *a* is used.

$$\alpha = \frac{v_f}{v_n} \tag{3.5}$$

4 Results and experimental verification

Using the layer deposition method de veloped above, experiments were carried out to investigate how the process parameters influence the layer periodicity length. Different values f or t he process parameters were investigated, shown in Table 1 below.

Table 1. Process parameters used in the experiments.

Process parameter	Min.	Max.	Remark
Nozzle diameter d_n	0.6	1.5	
	mm	mm	
Distance nozzle-	5 mm		
platform $h_{\rm nl}$			
Feed rate $v_{\rm f}$	0.03	0.08	
	m/s	m/s	

Nozzle outlet	0.09	1.06	
velocity v_n	m/s	m/s	
Concentration w	0.575		The solvation temp.
			acc. to figure 1 is T_s
			= 58°C
Temperature T_1	Approx.		Ambient temperature
	25°C		
Temperature T_2	Approx.		Depends on the heat
_	80°C		losses of the exp.
			system, shown in
			figure 2
Temperature T_3	60°C		Depends on the
			solvation temp. T_c

The r esults, i llustrated i n Table 2, r epresent t he predicted c ontiguous a nd non -contiguous a s well a s uniform and non-uniform structures of the deposited layers with r espect t o t he s peed r atio and t he distance between nozzle and the deposited layer h_{nl} .

Table 2. Experimental results of the structure of the depositedlayers for different speed ratios and distance between nozzleand the deposited layer h_{nl} .



As obs erved from t he t able, t he opt imum di stance between t he nozzle and the deposited l ayer h_{nl} can b e derived. The contiguous and uniform structure as in type 1 (figure 4) can be achieved at a specific speed ratio.

If the speed ratio has a value of 0.15 (type 1a: layered structure) or 0.35 (type 1b: dotted structure), this results in a uniform contiguous structure as r equired in an additive manufacturing process. Since type 1a has a layer periodicity length but type 1b does not, there must be a transition b etween these t wo types. This transition z one can be determined experimentally, which is illustrated in figure 6.



Figure 6. Measured and calculated values for the layer periodicity length.

There is a limit below which the measured periodicity lengths ar e n ot i n acco rdance with t he p reviously calculated lengths. This limit ranges from $a/d_n = 320 (m^{-1})$ to $a/d_n = 350 (m^{-1})$ and constitutes the transition zone. Above th is l imit, the measured v alues ap proximately conform with t he t heoretical v alues. T he s urface structures of t he d eposited l ayers b elow a nd ab ove t he limit differ significantly, as shown in figure 7. A layered structure (with n o p eriodicity le ngth) c an b e p roduced when a/d_n is lower than the limit. To produce a dotted structure (with a d efined p eriodicity le ngth), a/d_n must be higher than the limit.



a. Layered structure



b. Dotted structure

Figure 7. Different types of surface structures: layered and dotted structure.

The case s tudy p resented in t his p aper s hows eight primary p rocess p arameters, which affect the d eposited layers: feed r ate v_f , nozzle o utlet v elocity v_n , d istance between n ozzle and t he d eposited l ayer h_{nl} , n ozzle diameter d_n , temperatures T_1 , T_2 , T_3 and the concentration w. T heir effect of distance b etween nozzle and t he deposited l ayer h_{nl} , and b oth v elocities v_n and v_f on the layer periodicity length l_l was investigated in more detail.

Tests with d ifferent speed r atios d emonstrated th at producing a contiguous and uniform surface structure is only possible with a speed ratio of a = 0.15 or a = 0.35, which can be controlled by the feed rate and the nozzle outlet velocity.

While $a/d_n < 320 \ 1/m$ result in a layered structure using $a/d_n > 350 \ 1/m$ produces a d otted s tructure. For s the latter, the theoretical layer periodicity length c an b e calculated with a formula derived in this paper.

5 Conclusion and prospects

This paper has focused on additive manufacturing of salt hydrates. A new additive manufacturing process was developed, w hich i s ba sed on t he de position of a subcooled l iquid s olution. T his novel process h as be en named subcooled liquid printing (SLP) by the authors.

The a dvantages of using the SLP process is the possibility of pr oducing di fferent s urface structures b y changing t he p rocess p arameters d uring t he o ngoing manufacturing p rocess. T he u se o f s odium acet ate trihydrate aqueous solution provides a dditional b enefits, such a s no n-toxic b ehaviour a nd l ow-cost p urchasing. Therefore, t his ad ditive manufacturing p rocess i s especially suitable for school and university environment.

To develop this SLP process to full technical maturity, other process parameters such as the temperatures T_1 , T_2 , T_3 , and different concentrations w must be investigated. Since the s ize of t he manufactured o bjects depends significantly on t he s trength of t he material, f urther research in this area is also indispensable.

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