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

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Abstract. This paper presents the latest outcomes in the field of additive manufacturing. Some salt hydrates as printing materials provide many advantages (such as good availability and low toxic behaviour) compared to other materials, thus making them particularly suitable for specific applications. A layered deposition method for salt 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 market size of additive manufacturing has 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 individualization of products (mass customization) can now be realized without the need for considerable additional effort, and the time to market for new products has been significantly reduced [5], [6]. During the past few years, some additive manufacturing technologies, such as the FDM, SLM and SLA processes, have even been superior over conventional manufacturing technologies (e.g. mold making). For mold making in the case of highly complex geometry like undercuts, the question of demolding comes into focus. Solvation is one common method for removing the mold. With this 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 due to their low solvable temperatures. To utilize the advantages of additive manufacturing and salt hydrates in mold making, a new approach of additive manufacturing process is developed.

Recent study indicates that the outlining factors to 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 heating and domestic hot water preparation [9], solar heating systems [10], and radiant 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 attempts to address this lack of research in using salt hydrates for additive manufacturing processes.

2 Material

In this section, the materials involved in the newly developed approach have been described. The chemical composition and structure of salt hydrates and sodium acetate trihydrate has been elaborated. Further references have been given which illustrates their usage in this additive manufacturing process.

2.1 Salt hydrates

A salt hydrate is a crystalline salt molecule that is loosely attached to a certain number of water molecules. The properties such as solvation temperature and toxicity of a salt hydrate (e.g. sodium acetate trihydrate) depend on the crystalline salt molecule and the number of attached water molecules. Thus, they differ significantly. Sodium acetate trihydrate (SAT) is distinguished mainly by the good availability and the low toxic 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 of SAT and contains no water molecules. The binary phase diagram of SA and water, as shown in figure 1, provides information on the states of aggregation at different temperatures 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 aqueous solution can assume two states of aggregation: the stable solid state and the metastable (subcooled) liquid state (Liquid+SAT) is seen. This subcooled state of aggregation can be converted into a stable state of aggregation by a disturbance 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 study investigates the influence of temperature, concentration, and other essential process parameters on the properties of the deposited layers.

3 Process

In this section, the thorough process of sodium acetate trihydrate is elaborated. The experimental set-up of the process is elucidated which is followed by the classification of geometry of the deposited layer. A mathematical model is then described for the calculation of ideal periodicity length.

3.1 Experimental setting for depositing layers

An experimental model was set-up for analysing and testing the process. It consisted of heating and cooling systems, pumps, temperature sensors, and 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, SAT (crystalline white powder) and water (liquid) are mixed in a vessel (no. 1) at a ambient temperature (T_1) in a defined concentration w . Using 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 cool it down from temperature T_2 to T_3 , which is still slightly above the solvation temperature. Subsequently, the solution is ejected as drops or a jet from a nozzle outlet (no. 5). The temperature must be 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). While dropping onto the platform (distance h_{nl}) the solution cools down and turns into metastable (but still liquid) state (step 2). The metastable solution impacts on a platform (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 the temperature of the deposited layer 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 the geometry of the deposited layer

The deposited layer at the platform can be classified according to its geometry into contiguous and non-

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

Figure 4. Geometrical classification of the deposited layer

While uniform geometries (type 1 and 2) yield a regular and repeatable deposited layer, contiguous geometries (type 1 and 3) ensure bonded layer structures. To deposit both regular and bonded layers structures, 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 periodicity length l_l and the layer thickness t_l (illustrated in figure 4) are used. 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.

Figure 5. Classification of the deposited layer.

As can be seen in the above figure, the layer width is the maximum dimension of a deposited layer, when measured orthogonally to the feed direction. The layer thickness is the dimension in the direction of the nozzle outlet velocity. The layer periodicity length indicates at 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 uniform and contiguous layers structures (type 1 in figure 4) the layer periodicity length can be derived theoretically when the droplet is formed at the nozzle via the balance of forces. Also, this derivation can be 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.

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

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 the continuous flow rate of the solution generated by the pump is correlated with the discrete liquid drops separating from the nozzle, the layer periodicity length, expressed in equation (3.2), can be derived.

$$l_l = \frac{V_{drop} v_f}{v_n d_n^2 \pi} \quad (3.2)$$

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

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

Since v_n has a considerably lower dimension than the first term, it can be neglected. Hence, (3.3) can be simplified as shown in equation (3.4).

$$l_l = \frac{v_f}{v_n g} \frac{4 \sigma_s}{d_n \rho_s} \quad (3.4)$$

In equation (3.4), the density and the surface tension of the solution depend strongly of the concentration and the temperature [15], [16].

Furthermore, for the dimensionless speed ratio of feed rate v_f and the nozzle outlet velocity v_n , the given name α is used.

$$\alpha = \frac{v_f}{v_n} \quad (3.5)$$

4 Results and experimental verification

Using the layer deposition method developed above, experiments were carried out to investigate how the process parameters influence the layer periodicity length. Different values for the 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 mm	1.5 mm	
Distance nozzle-platform h_{nl}	5 mm		
Feed rate v_f	0.03 m/s	0.08 m/s	

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

The results, illustrated in Table 2, represent the predicted contiguous and non-contiguous as well as uniform and non-uniform structures of the deposited layers with respect to the speed ratio and the distance between nozzle and the deposited layer h_{nl} .

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

Speed ratio	$\alpha = 0.05$	$\alpha = 0.15$	$\alpha = 0.25$	$\alpha = 0.35$	$\alpha = 0.45$
Structure					
$h_1 = 5 \text{ mm}$					
Type	3	1a (layered structure)	3	1b (dotted structure)	2
$h_1 = 20 \text{ mm}$					
$h_1 = 50 \text{ mm}$					

As observed from the table, the optimum distance between the nozzle and the deposited layer h_{nl} can be 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 required in an additive manufacturing process. Since type 1a has a layer periodicity length but type 1b does not, there must be a transition between these two types. This transition zone 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 are in accordance with the previously calculated lengths. This limit ranges from $\alpha/d_n = 320 \text{ (m}^{-1}\text{)}$ to $\alpha/d_n = 350 \text{ (m}^{-1}\text{)}$ and constitutes the transition zone. Above this limit, the measured values approximately conform with the theoretical values. The surface structures of the deposited layers below and above the limit differ significantly, as shown in figure 7. A layered structure (with no periodicity length) can be produced when α/d_n is lower than the limit. To produce a dotted structure (with a defined periodicity length), α/d_n must be higher than the limit.

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

The case study presented in this paper shows eight primary process parameters, which affect the deposited layers: feed rate v_f , nozzle outlet velocity v_n , distance between nozzle and the deposited layer h_{nl} , nozzle diameter d_n , temperatures T_1 , T_2 , T_3 and the concentration w . Their effect of distance between nozzle and the deposited layer h_{nl} , and both velocities v_n and v_f on the layer periodicity length l_l was investigated in more detail.

Tests with different speed ratios demonstrated that producing a contiguous and uniform surface structure is only possible with a speed ratio of $\alpha = 0.15$ or $\alpha = 0.35$, which can be controlled by the feed rate and the nozzle outlet velocity.

While $\alpha/d_n < 320 \text{ 1/m}$ results in a layered structure using $\alpha/d_n > 350 \text{ 1/m}$ produces a dotted structure. For the latter, the theoretical layer periodicity length can be 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, which is based on the deposition of a subcooled liquid solution. This novel process has been named subcooled liquid printing (SLP) by the authors.

The advantages of using the SLP process is the possibility of producing different surface structures by changing the process parameters during the ongoing manufacturing process. The use of sodium acetate trihydrate aqueous solution provides additional benefits, such as non-toxic behaviour and low-cost purchasing. Therefore, this additive manufacturing process is 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 must be investigated. Since the size of the manufactured objects depends significantly on the strength of the material, further research in this area is also indispensable.

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