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The Line Formation with Alumina Powders in Drop on Demand Three Dimensional Printing

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Abstract

Three Dimensional Printing (3DP) is a Droplet-Based Manufacturing (DBM) process, in which powdered materials are deposited in layers and selectively joined with binder from an ink-jet style printhead. Unbound powder is removed upon process completion, leaving a three dimensional part. With this technology, functional parts or moulds (rapid tooling) can be created directly from a CAD file. Drop on Demand (DoD) is an emerging inkjet technology in 3DP, but it seems that the interaction between drops and powder grains cannot be explained with the available Continuous Jet (CJ) models. In this paper, an experimental theory describing the main physical phenomena involved is proposed. The role of the powder mobility is stressed and documented by pictures and observations coming from a systematic experimentation exploring a multidimensional variable space. A simple mathematical model to predict the line size and density is also proposed.

Keywords: Rapid prototyping, Physical model, Ceramic Powder

1 INTRODUCTION

Three Dimensional Printing (3DP) is a layered manufacturing or Solid Freeform Fabrication (SFF) technique known more as rapid prototyping [1] [2]. Parts are fabricated by the addition of layers, which are made of contiguous lines of powder grains selectively bound by an inkjet style printhead. Unbound powder is removed upon process completion, leaving a three dimensional part.

Continuous Jet (CJ) technology [3] has been traditionally used to print a liquid binder into a powder. More recently, the Drop on Demand (DoD) technology is earning a growing interest because it has preferred features for new applications where it is necessary to control the frequency drops are printed, like in vector printing, where the printhead speed is not constant.

3DP technology has been developed at the MIT [4] [5] using alumina as the powder and colloidal silica in ethylene glycol as the binder, like in the investment casting (or lost wax) process. With this technology, functional parts or moulds (Rapid Tooling) can be created directly from a CAD file [6]. Over the last decade, this potential has been exploited with different material systems, including metal powders. Special applications [7] include controlling the local composition [8], the microstructure [9] or the surface macrotexture [10].

Several authors [11] have investigated the interaction of binder and powder with CJ. The most powerful approach seems the direct observation. A droplet impact observation station based on high-speed imaging has been developed [12] and used in the case of single drops [13]. Straube [14] has also proposed a physical model of the drop-powder interaction during and after the impact in the formation of lines with CJ.

The application of the same method is not possible in DoD. For this reason a deductive approach has been

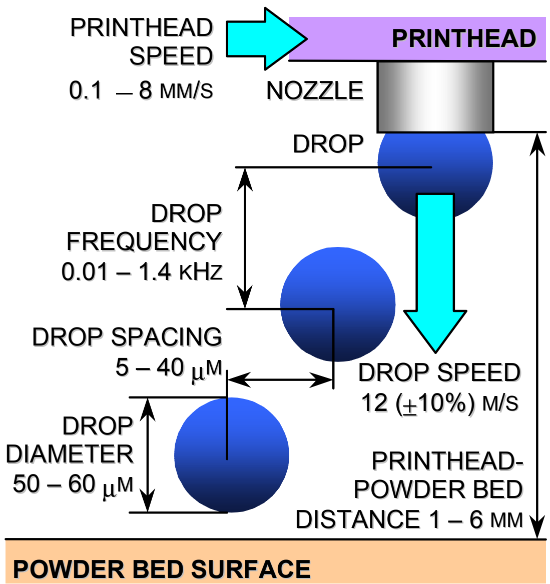

Figure 1: General scheme of the main process parameters in 3DP and range of the values available and tested with the DoD technology.

used. This paper represents the first systematic analysis of the line formation with the DoD technology. A theory to explain the basic phenomena in the binder-powder interaction is proposed. In addition to the main process parameters, the role of different variables has been tested and their effects are discussed.

2 EXPERIMENTAL TECHNIQUE

Individual drops and parallel non-touching lines, called in jargon respectively primitive balls and primitive lines, are printed in a bed of loose powder. -10, 20 and 30 μm spherical alumina powders have been printed using colloidal silica in ethylene glycol in a 50% (vol.) water solution as the binder. The minus sign refers to a powder whose size distribution is smaller than the nominal size. The other powders are single size. Several mixtures have been used, containing 2.5 and -5 μm platelet and 5 μm equiaxial alumina powders as additives in the range 10%-25% (wt.). The powder is spread manually and a commercial printhead is used, model 51626A from HP [15].

Tests have been carried with combinations of the main process parameters, exploring the whole range available with the used DoD printhead, indicated in Figure 1. The drop diameter has been calculated from the flow rate supposing a spherical shape. The actual drop shape depends on the printhead nozzle and varies during the flight to the powder bed, which should be kept to a minimum in DoD. The printhead speed and the drop frequency and spacing are related by a cinematic relationship.

3 THE LINE FORMATION WITH CJ AND DOD

A fundamental difference between the lines printed with the CJ and the DoD technology is their position within the powder bed. With CJ, the lines use to lay in a large trench and are completely visible. On the opposite, with DoD, lines are formed below the powder bed surface on the bottom of a deep groove. For this reason, direct observation as in [12] is not possible and a deductive approach has been followed. The completely visible lines shown in the pictures have been separated from the loose powder with an air jet.

The difference between CJ and DoD is due to the different entity of the powder ejection at the drop impact and is related to the higher turbulence of the binder inside the line. The main reason is probably the higher drop frequency (about 100 times) and higher drop size (about 50% more) than DoD, which produce a higher specific energy input in CJ. The lower kinetic energy in DoD with respect to CJ produces a lower or missing powder ejection. In addition to the binder turbulence and the powder ejection, the specific kinetic energy determines the drop penetration into the powder bed and the engulfing of grains after the impact.

The binder specific kinetic energy depends on the following parameters: drop mass/size and speed and drop spacing and frequency (Figure 1).

- The drop speed can only be controlled in the nozzle design phase and it is of the same order for DoD and CJ.
- Lower drop spacing and higher drop size have a negative effect on the line size and consequently on the process resolution, so they are limited.

The main consequence of the two points above is that the specific kinetic energy can be controlled only slightly and it is lower in DoD than in CJ; for this reason DoD has a different physical model, which is investigated here.

Another important consequence of the lower frequency in DoD is the negligible influence between successive drops. This allows considering the behavior of each drop individually.

4 THE PHYSICAL MODEL

The line formation involves the main interactions between a liquid binder and a loose powder. In 3DP, three phases are present and the interaction at their surfaces determines the process behavior [16]. The interphase region is studied by the Surface Chemistry, in the domain of the Physical Chemistry [17].

The penetration of grains inside the drop at the impact is determined by the dynamic pressure, which opposes to the force of Laplace, necessary to win the difference between the pressure inside and outside the drop. This difference of pressure is proportional to the binder surface tension, which is a molecular attraction towards the bulk of the liquid.

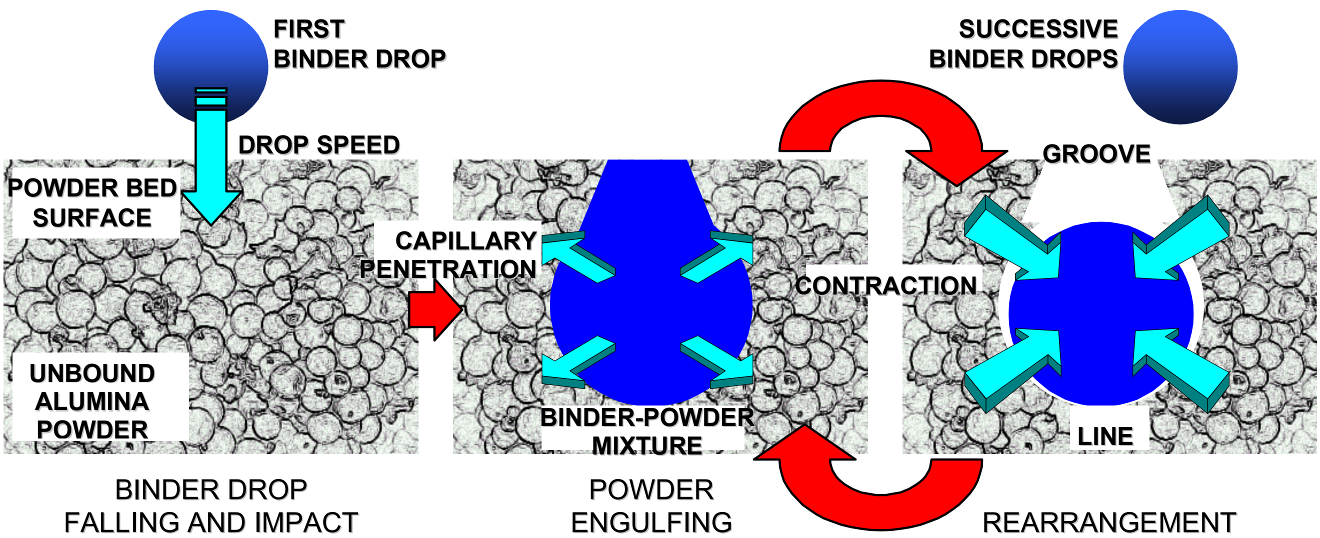

Figure 2: Scheme of the line formation with DoD. From left to right, after impact, the drop expands engulfing the powder. A groove is formed. An iterative process starts: penetration for capillary and contraction/rearrangement of the binder-powder mixture fed by successive drops.

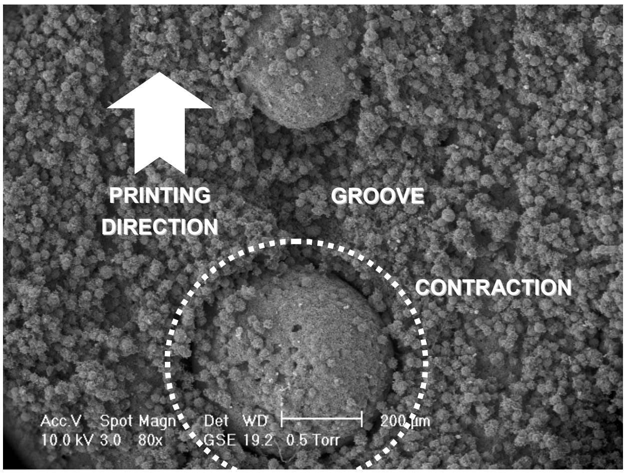

Figure 3: SEM image. Two primitive balls printed using 20 μm spherical with 25% (wt.) 2.5 platelet alumina powder. The groove between them is visible. Detail of the binder-powder mixture contraction.

The surface tension of a liquid has experimental evidence in the capillary effect, which also represents a practical method to measure it [17]. Other methods involve the thermodynamics or chemical balances considering the surface energy and the latent heat of vaporization respectively [16]. It is important to notice that the surface tension does not depend on the amount of liquid, because the molecular forces are short range [16].

After the kinetic energy has been completely dissipated after the impact, the interaction between the binder and the surrounding dry powder is determined by a relative property of the two materials involved, called wetting and first postulated by T. Young in 1805 [17]. It is usually expressed as the angle between the surface of the liquid and the solid. Alumina has good wetting with the two liquid components of the used binder: water and ethylene glycol. Water has high surface tension with respect to other liquids at environmental temperature (72.88 mJ/m^2), but it is reduced by the addition of several compounds, including the ethylene oxides [17]. The surface tension of a liquid is generally inversely proportional to wetting, as demonstrated by A.L.V. Dupré in 1869 [17].

A rough estimation of dynamic pressure and of the surface tension showed that they are about 1/2 and 1/10 of the Laplace force [14].

4.1 Hypotheses

The process (Figure 2) can be divided in the following phases, after the drop impact:

1. drop penetration in the powder bed and engulfing of grains;
2. rearrangement and contraction of the binder-powder mixture;
3. engulfing of grains from the line bottom.

Capillary penetration, rearrangement and contraction develop with a spherical and cylindrical symmetry respectively with primitive balls and lines. These radial effects of the phenomena mentioned above determine the ball/line diameter and shape. In addition, there is a preferential vertical direction for the initial drop speed and for the presence of gravity thereafter.

The momentum coming from the initial drop speed determines the drop penetration into the powder bed (Figure 2, center). The penetration depth depends on the initial kinetic energy, which is dissipated by the work of several forces, including:

- the force of Laplace, necessary for a grain to win the difference between the internal and the external pressure of a drop;
- the friction between binder and powder and other dissipative forces, in the rearrangement of the binder-powder mixture;
- the powder ejection;
- the compaction of the loose powder below.

Rearrangement of the binder-powder mixture takes place for the tendency of liquids to minimize their surface energy. This phenomenon is beneficial because a liquid free to move has the tendency to assume a round surface and this determines a smooth line surface. In order to minimize the surface energy, the binder-powder mixture volume is minimized too, by having the grains fill the available voids. The binder surface forces change the structure of grains inside the drop in order to minimize the volume and to assume a round surface (spherical or cylindrical).

The line contraction determines a separation of the line from the powder bed. It seems that an iterative process takes place between engulfing and rearrangement: new grains are engulfed from the line sides until the line is completely separated from the surrounding loose powder for the iteration of rearrangement and contraction.

The engulfed grains increase the drop size, so the binder reaches more grains. When the kinetic energy is completely dissipated, the drop penetration is determined by the capillary penetration of the binder among grains, which depends on the grain surface wetting by the binder. Wetting is very important for the adhesion to the previously formed lines and layers.

New grains are engulfed from the groove bottom on which the line is laying for the gravity force. The line weight is increased for the compaction and for the presence of the binder filling the empty spaces among grains. The different depth of primitive balls and lines within the powder bed shows the effect of weight: primitive balls are near the bed surface (Figure 3) while lines are progressively submerged for the addition of new binder from successive drops.

The process rests when any of the following situations is verified:

- no more binder is surrounding the line and no more

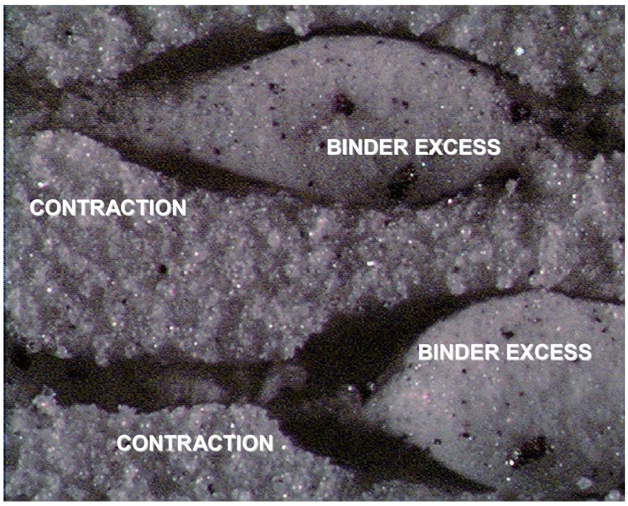

Figure 4: Two submerged parallel lines made with 20 μm spherical and 10% (wt.) -5 μm alumina powder. The binder excess has raised the powder from the grooves into two large and smooth bubbles. The contraction after rearrangement has a preferential axial direction.

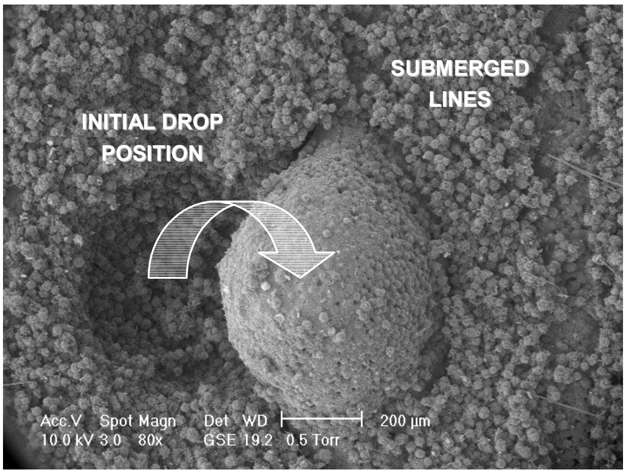

Figure 5: SEM image. 20 µm spherical and 2.5 platelet 25% (wt.) alumina powder. A primitive ball was reabsorbed by a contiguous touching line. The former primitive ball position is shown by an empty space.

external grains are reached by the liquid;

- the binder wets external grains but the attraction force is lower than the inter-grain force;
- the binder is dry.

After drying, the volume of the binder is reduced to a minimum and is only present in the necks among grains as shown in Figure 7.

From the described model, it can be concluded that the formed line is the result of the binder action and of the powder reaction. More details on these two contributions and examples will be provided in Chapters 5 and 6.

4.2 Experimental evidence

Proof of the smoothing binder action is the spherical shape of primitive balls (Figure 3) and the cylindrical shape of primitive lines. A smooth and round surface is shown in Figure 4 by the powder raise with an excess of binder. The excessive binder input has been obtained printing on a thin layer of powder spread over a non-absorbing medium. The absence of loose grains at the line bottom produced binder excess, forming the shown bubbles with powder.

An example of the effect of the binder penetration and rearrangement is given in Figure 5. The binder from the submerged line reached a primitive ball on the left. In

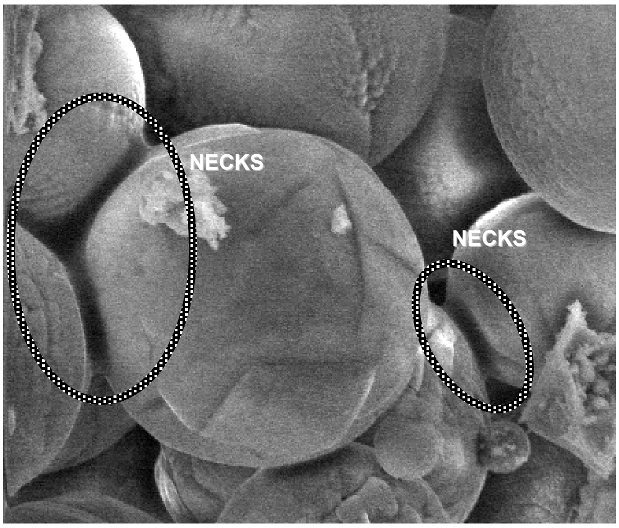

Figure 7: SEM image. The 20 µm spherical alumina powder used. Some impurities are present. The connecting necks among grains are outlined.

order to minimize the surface energy the powder contained in the lateral appendix, which was formed at the contact between the line and the drop, was reabsorbed in the line.

The necessary condition for a grain to be engulfed is that the inter-grain forces are lower than the attraction by the binder. An example of a single large grain attached to the external line surface is shown in Figure 6, with a detail of the good connection involving also the smaller grains.

Contraction of different entities has been shown in all experiments. An example is displayed in Figure 3. The powder compaction inside a line produces a higher density and consequently a higher structural resistance.

4.3 The axial binder movement

In addition to the phenomena described, which act preferentially in the vertical and in the radial direction, there is an axial movement of the binder in the forward direction. This is caused by the energy input coming from the addition of subsequent drops. More minor contributions in the same direction come from the following phenomena:

- the capillary penetration into the loose powder for the drop increase due to engulfing is omnidirectional, so there is also a penetration in the forward direction;

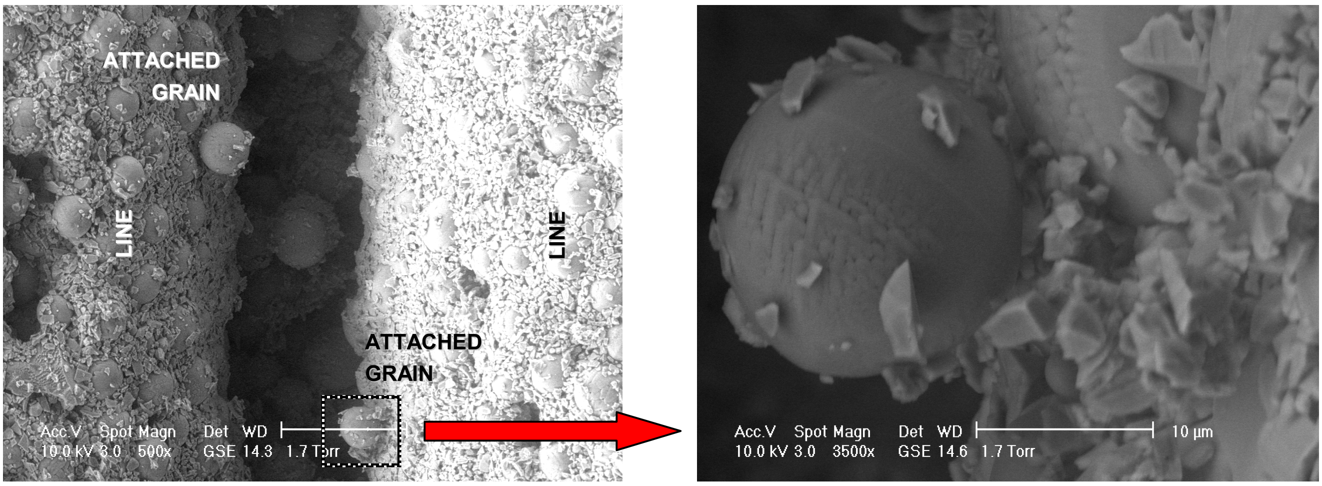

Figure 6: SEM images. 20 µm spherical with 25% (wt.) 2.5 platelet alumina powder. Attraction of single large grains to the external surface of the line (left) and detail of the connection (right).

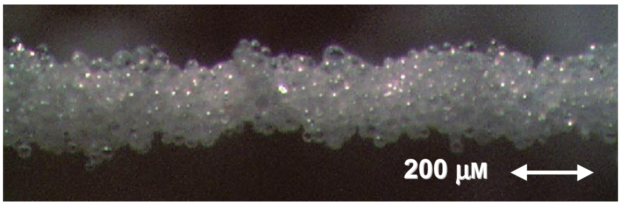

Figure 8: 20 μm spherical alumina powder. An irregular line printed at a high drop spacing (40 μm).

- the printhead speed is in the order of 1/1000 of the drop speed, but it still produces a momentum in the forward direction.

Some examples of the effects of the axial binder movement include:

- the groove generated between primitive balls printed far apart from each other (Figure 3);
- a groove is also produced in the case of line interruptions (Figure 10);
- the preferential contraction of bubbles in the axial direction (Figure 4).

5 THE BINDER ACTION

There are two types of interaction between binder and powder:

1. engulfing. Several grains are simultaneously invested and surrounded by a large amount of binder;
2. capillary penetration. Grains are reached individually.

Engulfing occurs at the drop impact and stops when the kinetic energy is completely dissipated. At this point, capillary starts, facilitated by the grain surface wetted by previous drops.

With both phenomena the binder rearranges the powder, but by acting on more grains, the rearranging effect is more evident during engulfing as enhanced in the following two typical situations.

- The top and the bottom of a line are mainly affected by the two different phenomena respectively. The lateral view of a line (Figure 9) shows the smoothing effect on the line top due to the high amount of liquid, while the bottom is more irregular for the addition of single grains reached for capillary.
- The drop spacing influences the binder input per unit of surface and consequently the prevalence of one of the two described phenomena. The effect of drop spacing is clearly visible as more irregular grains distribution at higher drop spacing (Figure 8).

Considering that wetting is inversely proportional to the surface tension (as explained in Chapter 4), engulfing is inversely proportional to the rearranging force.

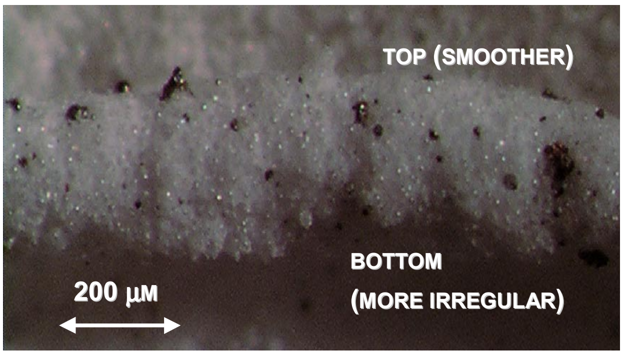

Figure 9: Lateral view of a line printed using 20 μm spherical with 10% (wt.) -5 μm alumina powder and metal powder impurities. The powder bed has been tapped.

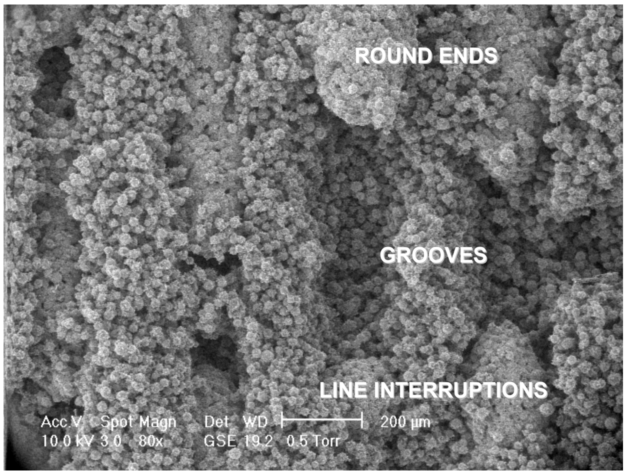

Figure 10: The groove presence is evidence of the axial movement.

6 THE POWDER REACTION

The powder reaction depends on the inter-grain forces determined by the following factors:

- Grains **shape**. The previous experience shows that better lines are obtained using equiaxial powders. The equiaxial shape (including the spherical shape of the used powders) ensures the highest mobility.
- Powder bed **density**. The powder size distribution and shape determine it. It can be increased by compaction (Figure 11).
- **Friction**. It depends on the inherent material friction, on eventual surface treatments and on the temperature.
- Miscellaneous **sticking** effects. They are mainly due to the environmental humidity, acting especially on the smaller grains for capillary. They may also be due to the presence of dirt or electrostatic forces.

The inter-grain forces are important also after a grain has been engulfed, because they influence the rearranging process as well.

According to the described model, the mobility of grains is fundamental in order to allow the binder to engulf new grains and to rearrange them. This statement will be experimentally proven in negative, by showing the effects

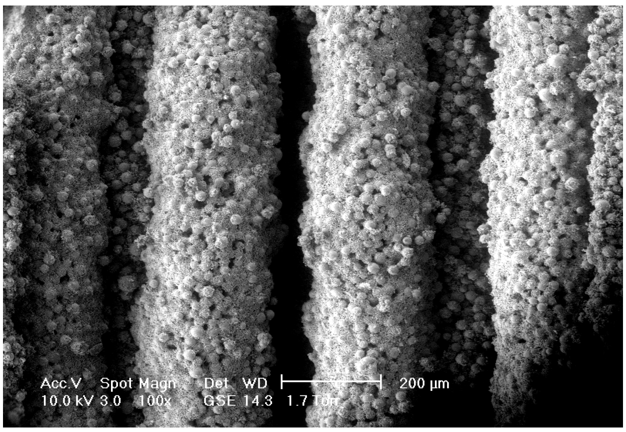

Figure 11: SEM image. 20 μm spherical with 25% (wt.) 2.5 platelet alumina powder. The negative effect of compaction is shown by the irregular external surface.

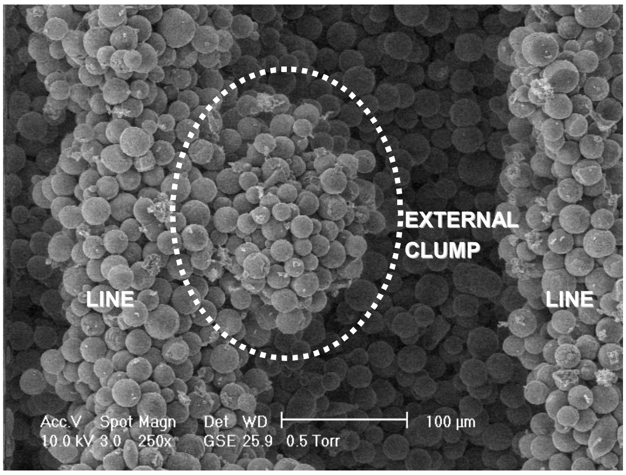

Figure 12: SEM image. 20 μm alumina powder. The left one of the two lines displayed has an external clump.

of reduced mobility.

A limit case is considered, the presence of a clump, which represents the lack of mobility, being grains stuck to one another. The grains clumping (Figure 12) is due to the presence of humidity or other sticking effects for the presence of dirt.

A clump can be a group of grains already stuck to each other before printing or it can be generated by a favorable capillary binder penetration into that group of grains.

The external part of a clump near the line surface can be attached to the powder bed. The interaction between a clump and the surrounding loose powder may prevent it from being completely or partially engulfed (Figure 12). A clump may remain segregated from a line and influence the binder behavior (Figure 13, top left).

A clump inside a line may affect the line regularity depending on the clump size and on the binder action. The line in Figure 13 (top right) has a relatively smooth surface, but its width is irregular. The binder may determine a smooth transition around it (Figure 13, bottom).

7 INCREASING THE GRAINS MOBILITY

The following techniques have been tested to increase the powder mobility: coating the powder and heating the powder bed. The two methods cannot be used simultaneously because most coatings, which have a polymer nature, irreversibly loose their properties at high temperature.

Coating the grain surface

The main intended purpose of coating powders is to reduce the surface friction through the addition of a polymer, which use to have a lower friction coefficient than alumina, but the friction reduction depends on the grain roughness before and after coating, so a thin coating (only a few molecules thick) is to be preferred. The additive quantity depends on the availabe surface and consequently on the powder size.

The tested additives are commercial surfactants used in a water solution. For the preparation, the powder is submerged with a known solution quantity. The additive weight is referred to the powder weight, because the solution is completely dried. The compact mass obtained is then shredded and sieved to completely separate all grains.

The best results have been obtained with a 0.3% (wt.) of Darvan C. On the opposite, a 7% (wt.) of Darvan C produced additional sticking effect, particularly after heating the powder bed for the polymerization.

Large binder drops (about 0.1 mm) deposited manually on the powder bed surface have been observed at the optical microscope. If small grains (< 5 μm) are present in the powder, their mobility is greatly increased for the reciprocal repulsion effect produced by the surfactant after coating. Smaller powders can also have a Brownian motion due to the statistical collision of the binder molecules [18].

It can be concluded that coating acts both on the dry powder among a grain being engulfed and the surrounding ones and on the wet powder during rearrangement inside the line (for the friction reduction and the repulsion effects).

Heating the powder

The effect of heating the powder is mainly to eliminate moisture, which is naturally absorbed by the small particles from the environment, and to reduce the grain friction.

The powder bed temperature has been increased in two ways, with an external lamp and heating the powder bed support. The first method has the disadvantage that the printhead is also invested by the radiating energy for the small distance from the lamp, and the nozzle and binder properties (viscosity, etc.) are also affected. Comparative tests printing on the same bed at different temperatures (room temperature, 50° and 180° C) have shown that the lines printed at higher temperature are more regular.

The angle of repose

A direct observation of the powder bed after spreading and after printing is not able to provide information on the powder mobility. No correlation has been found between line quality and the appearance of the powder bed (e.g. the powder bed surface, the groove shape, etc.). Very similar beds have shown a radically different behavior when exploring the lines using an air jet.

In addition to printing tests, the effects of the surface treatment and of heating on different powders have been assessed with a laboratory test: measuring the angle of repose. This specific test to estimate the powder flowability has shown the positive effect of both methods, as an angle reduction. The actual powder temperature has been directly measured with a thermocouple during printing and before and after the test.

From the data reported in Table 1 it can be noticed that:

- coating and heating are both beneficial;
- the addition of smaller powder reduces the powder mobility;
- larger powders have a lower mobility.

It is not known if heating influences only humidity or also friction. It is probably mainly due to humidity.

8 DROP SPACING AND LINE DENSITY

The maximum theoretical drop spacing to print a line is given by the size of the primitive ball. In experiments, it has been observed however that there is a maximum drop spacing, related to the minimum amount of binder to trigger the phenomenon off, which is about 25-30 μm for the different powder mixtures tested. Apparently, there is no minimum value, apart from the productivity constraint.

Closer droplet spacings make larger lines, as it can be understood by the volume of material, but this is not desirable in order to achieve a higher detail on the final part. Lower drop spacing corresponds to a higher amount of liquid.

Supposing a uniform density of the powder bed and a uniform distribution of the binder, there is the following geometric relationship between the line diameter D_{PL} and the drop spacing DS:

$$D_{PL}^2 = \frac{K}{DS} \tag{1}$$

Using experimental data, the density ρ_{PB} of a primitive ball and ρ_{PL} of a line can be estimated. ρ_{PB} and ρ_{PL} can also be considered as the percentage of space left free by the liquid inside a primitive ball or line.

$$\rho_{PB} = 1 - \frac{V_D}{V_{PB}} = 1 - \left(\frac{D_D}{D_{PB}}\right)^3 \tag{2}$$

being V_D, the volume of a binder drop of diameter D_D and V_{PB}, the volume of a primitive ball of diameter D_{PB}.

Using typical values,

$$\rho_{PB} \cong 80\% \tag{3}$$

Considering that the tap density (about 60%) is the upper limit for real powders, it can be concluded that the volume of voids is about 20%.

Regarding the primitive line, in a line section S_{PL} of diameter D_{PL}, the binder input is

$$S_B = \frac{V_D}{DS} = \frac{1}{6}\frac{\pi D_D^3}{DS} \tag{4}$$

$$\rho_{PL} = 1 - \frac{S_B}{S_{PL}} = 1 - \frac{2}{3}\frac{D_D^3}{\left(DS \cdot D_{PL}^2\right)} \tag{5}$$

substituting from (1)

$$K = DS \cdot D_{PL}^2 \tag{6}$$

we obtain

$$\rho_{PL} = 1 - \frac{2}{3}\frac{D_D^3}{K} \tag{7}$$

and also

$$K = \frac{2}{3}\frac{D_D^3}{\left(1 - \rho_{PL}\right)} \tag{8}$$

The expression (8) shows explicitly the dependence of the factor K in (1) from the drop size and the powder density of the formed line.

A simulation has been performed using the expression (7) in the case of a 20 µm spherical alumina powder. With two different drop sizes D_D (50 and 60 µm) and K (480,000 and 350,000 µm^3), we obtain

$$\rho_{PL} \cong 80\% \tag{9}$$

This result shows that the available space among grains for lines is of the same order of the primitive drop free space, from line (3).

(3) and (9), which have been obtained using simple geometric considerations and experimental data, show that the estimated theoretical space left free by the liquid inside the primitive ball and the primitive line are of the same order (the density was about 80% with the tested powder). It can also be noticed that they are both higher than the maximum practically achievable density (in both cases, the volume of voids is at least 20%). In the previous chapters, it has been shown that the presence of voids is beneficial to the powder rearrangement for the higher freedom of grains.

With the simple hypotheses used, a generalized application of the above expressions, in particular (2), (5), (7) and (8), is not reasonable. However, they are useful to

Table 1: The angle of repose of the tested powder mixtures at room temperature and after heating. When not indicated, the error is ±1°.

Powder	*Room Temp.*	*Hot 70-90° C*	*Remarks*
Al 20	37.5 ± 1.5	23.5 ± 1.5	
Al 20	38 ± 2	32 ± 2	Coated with 0.3% (wt.) DarvanC
Al 20	38 ± 2	sticking	Coated with 7% (wt.) DarvanC
Al 20	52	53	+ 20% (wt.) -5 µm
Al 20	50	49	+ 12.5% (wt.) 5 µm equiaxial
Al 30	41 ± 3	NA	

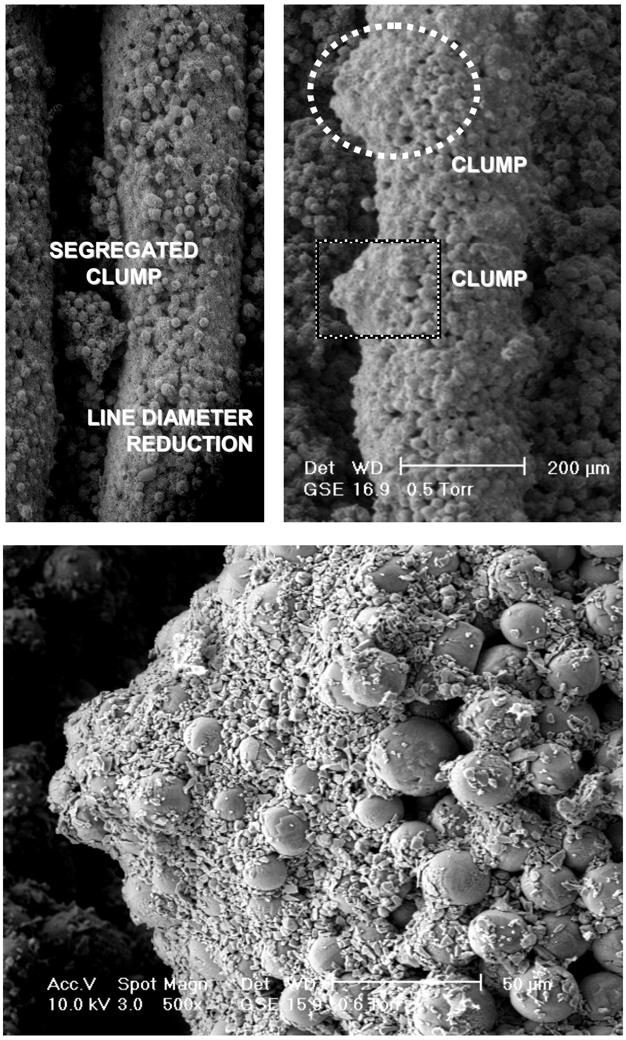

Figure 13: SEM images. 20 µm spherical and 2.5 platelet 25% (wt.) alumina powder. An external clump (top left). Example of irregular line diameter due to internal clumps (top right). Detail (bottom) of the clump incorporation and of the smooth powder transition.

predict small variations of some of the indicated parameters by measuring the others.

9 SUMMARY

An experimental deductive theory of the line formation in the DoD 3DP of alumina powders has been proposed. It can be directly applied in production to improve the line quality. The main differences with the CJ models have been described. According to this theory, in the line formation, the powder grains are rearranged under the liquid binder action, which is beneficial for the line quality for the natural tendency of liquids to assume a smooth and round surface. The powder mobility directly influences the rearranging process and for this reason it should be increased. Several parameters influence the inter-grains forces and their effects have also been described in the paper. A simple mathematical model to predict the line size and density is also proposed.

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