AN EXPERIMENTAL MODEL OF THE LINE FORMATION AND A NEW APPROACH TO THE OPTIMIZATION OF THE LINE QUALITY IN THE DROP ON DEMAND THREE DIMENSIONAL PRINTING OF DRY POWDERS

by

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ABSTRACT

The main purpose of this study is to improve the surface finish of dry powders in 3DP.

The process optimization is achieved focusing on the basic elements, the so-called "primitive line". Obtaining good lines is a necessary condition to have good surface finish, geometric tolerances and mechanical resistance.

From the assembly of lines, layers are obtained and from the addition of layers, a complete part can be manufactured, with all the benefits of the so-called rapid prototyping (RP) or solid freeform fabrication (SFF) or layered manufacturing (LM) techniques. In 3DP, one of these, originated and under study at the MIT, a binder is selectively printed using an inkjet printhead on each layer of the part, which is made of a powder bed. After removing the loose powder, a functional part is obtained.

The target application of ceramic parts manufactured with the technique examined in this study is the casting of metals according to the process known as lost wax or investment casting (rapid tooling). Among other 3DP applications, the direct fabrication of metal powders is also possible.

A new approach for the process optimization with new material systems is described in this report. It has been successfully applied both to metal and alumina powders.

Numerous tests have been carried out to assess the effect of the main process parameters on the line quality and to point out the more relevant ones in improving the line quality.

The main details of building an experimental facility are described. To print lines the following tasks have undergone: mechanical and electronics set-up, and software development.

In addition to the main issues in the material and printhead characterization, a new simple method for the drop speed measurement is described. An overview of the main critical aspects of standard laboratory tests and new proposed techniques is also provided.

The proposed approach includes the characterization of the defect morphology, analysis of possible causes and remedies. More than ten defect types have been identified. However, the classification can be extended for new material systems or printing conditions and even to other processes involving the formation of lines and the presence of powders, like Selective Laser Sintering. By defining defects, the line quality is also defined. This allows the researcher to have an instrument to understand results of experiments or for the technician to objectively identify a problem and provide a solution from previous experience. This is also a standard method the collect and share knowledge.

The main interactions that occur between binder and powder in the line formation are addressed. The surface quality of the final part directly depends on them. From the analysis of all the quantitative and qualitative data collected according to the proposed method, an interpretation of the main phenomena occurring in the line formation is proposed. A theoretical model that includes all the observed phenomena and to describe the interaction between the binder and the powder is proposed. Progressing in the 3DP process comprehension is a key to extend the range of applications, and to improve reliability and performance.

An innovative aspect of this study, with the given material systems, is the particular drop on demand (DoD) printhead used, which is based on the thermal effect to make drops as opposite to the piezo principle of the traditional Continuous Jet (CJ). In this feasibility phase, a commercial printhead has been used. An important advantage of DoD is the better performance in vector printing, which represent the next generation of 3DP machines.

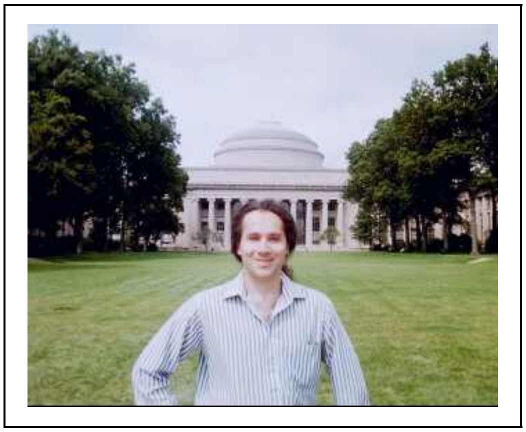
The details of a new 3DP beneficial technique are also provided: the multi-pass method.

DEDICATION

To my wife Serena,
Who entertained my daughter Clara in the long days I was working.

To my daughter Clara,
Who entertained my wife Serena, while she wanted to work on her project.

ABOUT THE AUTHOR



Michele Lanzetta was born in Rome (Italy) on March, 17th 1966, he is Assistant Professor at the DIMNP, the Department of Mechanical, Nuclear and Production Engineering, of the Faculty of Engineering of Pisa University since 1998.

He has been visiting the MIT supported by the Italian CNR (the National Research Council) and the DIMNP for the summer of 2000.

During his doctoral studies in Industrial Automation and Robotics, achieved in 1997, he spent the summer of 1996 as a visiting researcher at the Computer Vision Laboratory, at Stanford University, Palo Alto (CA) with a fellowship from the Italian CNR.

In 1993 he attended the Master in Management of Innovation from Scuola S. Anna of Pisa and developed his Project Work at Fase (Piaggio group).

To get is Master Degree in Aeronautical Engineering (achieved on April, 10th 1992 from Pisa University) he developed his final project at Sup'Aéro, École Nationale Supérieure de l'Aéronautique et de l'Espace in Toulouse (France), supported by an Erasmus Project fellowship (April to December 1991).

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I would like to mention Prof. Michael Cima for the useful suggestions at the weekly meetings and all the other members of the Ceramics Group from the Material Science Department.

A great lesson comes from the winning MIT approach to research (…if I do, I learn). I think I have *done* a lot of (new to me) things.

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Chapter I.

INTRODUCTION

What is 3DP

Over the last ten years, a new class of fabrication techniques has emerged, which goes by the names Rapid Prototyping (RP), Solid Freeform Fabrication (SFF) or Layered Manufacturing. These techniques include Three-Dimensional Printing (3DP), Selective Laser Sintering (SLS), Fused Deposition Modelling and Stereolithography. In [Sachs00] the evolution from prototyping to production is stressed for the inherent advantages of the layered method.

Three Dimensional Printing (3DP) is a rapid prototyping process in which powdered materials are deposited in layers and selectively joined with binder from an ink-jet printhead. The evolution of the 3D Printing technology is characterized by many steps. Every of these represent a significant innovation in terms of process, but also significant changes in terms of machine design and configuration.

The main advantage with respect to the traditional methods is the inherent Layer Addition method that allows making parts of any shape, including internal voids, undercuts and overhangs that would simply be not feasible.

The target application and criteria for the selection of the material system

3DP allows both direct metal and indirect mould fabrication (rapid tooling).

The contingent target application of the examined process is making ceramic moulds for the investment casting of turbine blades of new generation[1]. A very good surface finish is required by this application so in this paper the new material system is studied, looking for the perfect line, which is the basic element of a 3D part.

Casting provides tight constraints regarding the materials to be used. In addition to other materials (metal powders), whose behavior has also been examined to understand the on-going phenomena, the following alumina powders have been used and have yielded the best performance: spherical 20 and 30 microns.

Among ceramic materials, the "spherical" alumina powder has been selected because it is supposed to provide better quality (smoother lines) through a more regular distribution of grains. The size distribution should contain a prevalence of at least 20 μm grains, because smaller grains tend to sinter during firing, causing shrinkage and consequently a worst dimensional control. A higher grain size (e.g. the 30 μm which is also available at the Lab) is not able to provide the required resolution.

Of course there is a drawback using spherical powders with respect to the -28 platelet, which is largely used on the Alpha Machine: the cost per kg is around 300 $ compared to the 10. So spherical powders target application is the casting of valuable products with high surface finish requirements.

Numerous tests have been carried out to assess the effect of the size distribution on the quality of a line.

The binder that is selectively printed must contain silica in order to make refractory shells. Colloidal silica has been traditionally used for centuries in the analogous process investment casting (or lost wax) and it is printed here as a suspension in ethylene glycol in a water solution.

More details on the material selection and their behavior are provided in the report and in appendix.

Questions?

This report tries to answer to direct questions: some simple ones that the author had before starting this research, by reading the related literature and the questions that

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[1] The moulds for special turbine blades from Allison, the engine manufacturer, with internal cooling channel can only be manufactured through layered manufacturing techniques. In this partnership 3DP is used.

arose during his work. Probably, now, at the end of this work, there are more fundamental open than answered questions; this shows that this topic is very alive.

Just to stimulate curiosity, the following simple questions and answers can be found in implicit and explicit form in this report:

- ☐ What are the main inkjet technologies? And the main differences? Why using a drop on demand printhead?
- ☐ What are beds, drops, lines? What numbers (dimensions, physical properties, etc.) are governing 3DP?
- ☐ What are the main process parameters? What are the controllable ones? What are their effects?
- ☐ What are the main physical phenomena involved in the process? And the main material properties?
- ☐ What are the typical laboratory tests in 3DP?

State of the art

All 3DP reports and papers available up to now are relevant to this study, because different material systems have many common phenomena. And fortunately most (all) related know-how has been developed and still alive in the people working in the 3DP Lab at the MIT. Regarding the printing of alumina powders there are two very recent projects: [Straube00] and [Werner00]. They used respectively a CJ and a DoD printhead.

The works from [Straube00], [Fan95], [Curodeau95] and [Bredt95] deal with a CJ printhead. The DoD printhead used has the following main differences with respect to the CJ (also see the chapter later on “the printhead characterization”):

- lower frequency;
- smaller drops;

Another important difference is the binder used, the binder B, with the addition of citric acid to reduce bleeding, instead of a water solution of colloidal silica in ethylene glycol.

The picture provided by [Straube00] coming from a long series of observations, though not complete, has been very helpful for the interpretation of several results. It also includes some theoretical calculations related to the drop-grain interaction. Specific information is also reported below in the chapter describing the proposed theoretical model. [Straube00] studied the line formation in the case of slurries and dry powders using ink and colored water for the observations with the observation station developed by [Fan95].

Previous similar analysis with the acquisition of high-speed images was performed by [Fan95] and was limited to single drops and to the impact with the bed.

[Werner00] also used a DoD printhead. He made tests with a commercial piezo printhead as opposed to the thermal or bubble jet printhead used in this study. The drop or impact speed in that case is about one order of magnitude lower. This is probably, but not definitely, the main reason for the mediocre quality of lines printed with alumina powders. According to [Fan95], the drop speed (or impact velocity) in the range 4 to 9 m/s affects the penetration depth of a 30%.

The most related work for the same methodology used regards a different material system [Baker97]. The main interest of [Baker97] comes from the very good performance achieved on stainless steel.

Another positive experience related comes from [Bredt95], which is an extensive study, including a series of experiments on different powder mixture with some interesting interpretations of results. The SEM image of a part of a line of very good quality obtained by [Bredt95] has been a spur in this project[2].

Additional useful information on the process was found in [Curodeau95].

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[2] The picture has been exposed on the workbench during the entire project, in the manner of a skull for monks until its quality has been surpassed.

The surface finish and the line formation of structural ceramic parts have also been studied in the case of small powders deposited as slurry [Knezevic98]. Both for the powder size and for the presence of a bed already containing a liquid, the process is very different.

From current project, two scientific papers have been written: [Lanzetta00] and [Lanzetta01]. They are a suggested reading before this report. They contain additional observations and data, and in some parts they integrate and complete this report

Description of the methodology used

Learning from experience

From the analysis of the approach used in this study, a general methodology can be extracted. It also takes into account some possible improvements with respect on how this project was actually developed.

The main differences regard the data collection. The synthetic message is: take as many data as possible!

In the first stage, considering the short duration of this project, the main purpose was the improvement of the 3DP performance with the given material system: the dry alumina powders. Many tests have been carried out trying to investigate many different situations, betting on **serendipity**, in order to get “the perfect line”.

Afterwards, considering the large number of experiments, this study has turned into a wide-ranging work: trying to understand more on the process, in order to have a more reliable definition of the plan of the additional experiments. For this reason, from the first phase the work was more focused on the **quantity** of experiments, while in the remainder each experiment has been accompanied by the collection of more data and observations.

Collecting data is a time consuming activity and *a priori* it is not evident what are the important or the necessary ones. This report gives an answer about “what” and “how” data should be collected in order to achieve the same purpose of this study on a new material system: improving the line quality.

Outline of the proposed method for the optimization of the surface finish of lines

The proposed method is based on the following steps:

1. Planning of experiments with the different variables.
2. Data collection. Characterization of the hardware and of the material system to predict the process performance. It is important to save pictures to have an objective identification of each situation. They should also be comparable (e.g. taken in the same position, with the same magnification, and lighting). Images should also be accompanied by the all the available process parameters and variables and by notes regarding qualitative observations (e.g. on the powder removal, the line depth within the bed, etc.).
3. Direct observation to assess the process performance. It is based on the observation of lines through an optical or scanning electron microscope of lines printed in different conditions. The analysis and interpretation of uncommon situations is also very useful to understand the main phenomena. A powerful aid for the interpretation is the proposed classification, in its present form or as a general tool.
4. Analysis and interpretation of data. A speculative task.
5. Building a theoretical model and or a classification of events.
6. Decision. Feedback to the decision tree.

The emphasis on the line formation

An innovative aspect of this approach to the 3DP optimization is the emphasis on the line.

Why focusing on the line?

The main target of this project is to determine the main process parameters and variables in order to obtain the best possible line with the given material system. We focus on the line formation, because it involves the main interactions between powder and binder.

The "primitive line", as it use to be addressed in jargon, is one of the basic element of a three dimensional object. Good lines are probably a **necessary** condition to have a good surface finish. The line surface is also the final product surface, so the line quality directly affects the surface quality, and, of course, the geometrical tolerances, of the final objects. However, this is not **sufficient** condition. Good lines mating (layers) and good layers mating should be insured further. This will be the task for the future project developments.

Why optimizing lines?

With some material systems, it is only sufficient to "make" a line, whatever it is. But 3DP of alumina powders is already state of the art, so the main purpose is here to go further and optimize the process and understand the main phenomena involved.

Extension of the method

This concept can be extended to layer and three dimensional part formation, in the sense that is always possible to debug a different case with the same approach: analysis of defects, possible causes and remedies.

Report outline

The structure of this report is simple. It does not represent the actual sequence of events during this project, but it is more divided in:

- What do we want and why? 3DP perfect lines!
- What instruments do we have? A certain hardware, software and material system.
- Results. How we got it!

It is supposed to be readable in random sequence. In the available time, I tried to put as many cross-links as possible and various indexes.

There are also obvious abbreviations, symbols and definitions in appendix, because they were not so for me at the beginning of this project.

Description of the main activities and timing of the project

The project officially started on May, 19th of 2000 and ended on October, 29th (>5 months).

The average time spent on this project has been:

- ☐ 7-8 hours/day for the experiments, the hardware set-up, and the software development at the laboratory, plus
- ☐ 2-1 hours/day for reading papers, planning the activity, and taking notes of results at home

on all days excluding weekends and vacation.

Table I - Outline of the main project activities

Timing	*Tasks*
May:	study of the bibliography and more detailed definition of the topic.
June:	electronics assembly; development of the 3Dring configuration; software development and first version of the last release available; hardware and software debugging and characterisation; random tests on different material systems.
July:	development of the 3DLine configuration; software modification and latest version available; specific tests on the effects of the printing parameters; the multi-pass method.
August:	experiments in different changing conditions, mainly changing mixtures, powder treatments, and spreading; powders characterisation; analysis of data; development of the classification of defects.
September:	validation of the best results; theoretical model; vacation.
October:	ESEM images and more data collection; report and papers editing.

Chapter II.

THE LAB TOOLS

Basic tools

Some of the basic tools are shown in Figure 1. Using a lot of tape and glue to assemble mechanical parts and using crocodiles for the electronics is probably a sign of precariousness, but it is also a good way to frequently change the system configuration and keep a high productivity.

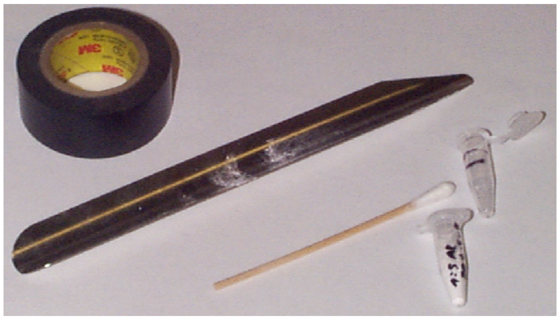


Figure 1 - Some basic laboratory tools

Tape was also used to attach the bed supports, usually a thin ceramic plate or a piece of paper, to the printing machine. Blades (Figure 33 of page 97) are available everywhere and can be used to cut the tape instead of trying to unstick it after printing, because the sudden detachment risks to spoil the sample.

Other typical instruments are:

- a syringe (Figure 33 of page 97), used to refill the printhead cartridge or to have readily a small amount of demineralized water for cleaning nozzles;
- the cotton tip displayed is typically used to clean the nozzles;
- the spoon displayed was used to pour the powders when making mixtures, or onto the bed support before spreading, to collect powders after sieving or to put them in small test tubes, like the ones displayed, used to measure the powder density.

Spreading the powder

Powders have been manually spread. The disadvantage of this method is the lower density and less regular distribution achievable with respect to an automatic machine.

A stainless steel bar with 5 mm diameter and 15 cm long was used to spread the powders. Between passes, and always before the last pass, it needs cleaning (with a dry paper), because the powder stuck to it changes its outline and makes a bed with grooves. For this reason, in order to offer always a clean surface to the bed, it is passed counter-rotating.

With some more sticky powders, like those containing 1 or 2 μm powder, a blade has also been used for spreading, but beds were always of lower quality.

Data collection: measurements

The remainder of this chapter and the two on the hardware and the material characterization represent the collection of quantitative data for the prediction of the process performance in the methodology described.

Investigation tools

Direct observation of drop absorption

A very useful method for understanding the possible interactions of drops and grains is manually putting a single drop with a syringe on a heap of powder. This test involves different phenomena with respect to 3DP because:

- drops are usually much bigger, 2-3 mm instead of 50-80 μm;
- they do not have the same speed and consequently a momentum that helps penetrating into the bed.

This test is useful mainly for two reasons:

- to give an indication through a visual perception of the main phenomena;
- as qualitative test with different powders and liquids, to have a comparative characterization of properties, such as wetting ability, capillary, etc.

For instance, the following observations have been useful.

- The **small particles** are engulfed later than the larger ones. It happens like when you add a cocoa powder into a cup of milk, it takes some time to be engulfed. If milk is hot, the engulfing is faster. The small grain shape has also an effect in this phenomenon. It seems that the round ones are engulfed faster than the platelet. This observation is important for the different behavior of grains in the powder mixtures used during printing.
- Water has a stronger **capillary** effect than colloidal silica in ethylene glycol. Absorption is even faster if a drop is put on powder wet with the same liquid. For large drops, capillary is more relevant for the absorption of the large liquid mass in the powder bed. For printed drops, the surface tension is higher than capillary, so they tend to remain where they are after the initial penetration.
- Among all the tested powders, only the -15 μm 316L stainless steel coated by [Baker00] appeared to be non wettable by water. Several drops deposited on it did not penetrate. The powder instead suddenly covered the whole drop surface. On the opposite, a drop deposited on the following powders was rapidly absorbed: the same uncoated metal powder, 20 μm spherical alumina, -10 μm alumina, 1 μm, and a couple of others alumina powders.
- When one drop of water containing 0.03% and 1% vol. of Darvan C has been added to a 1 μm alumina powder, it has been clearly observed that the engulfing of grains is associated to a fast and continuous movement inside the drop. This is due to the action of the surfactant, that make the small grains repel to each other. The same has happened partially with the -10 μm alumina, probably to the smaller grains only. No movement has been noticed with the 20 and 30 μm powders. The observation lasted several minutes. It is possible that after the entire surface of small grains has been coated they stopped because the motion is due to a different surface charge. If instead, the motion were due to repulsion, the particles would not stop moving. What happen after several minutes is interesting for speculations only and it is not relevant for the process, because at that time the line is already dry.

The effect of gravity on (large) drops

Both large and small single drops made with a syringe have a quite spherical shape. Gravity is not able to flatten them and this shows that its effect is negligible with respect to the surface tension.

Regarding the gravity effect on the powder, both large and small grains tend to fall to the drop bottom when they are inside. Exceptions are the mentioned action of the surfactant on the small powders keeping them in motion and the case of small grains and non wettable coated grains, which remain outside the drop, surrounding it all for their low tendency to be engulfed.

Observation at naked eye

Considering the small dimensions involved, all the observations require the use of a microscope. The human eye is able to percept details of the order of the grain size, like the regularity of spreading a bed.

After printing, the regularity and depth of grooves can be assessed.

For smaller powders, the presence of clumps caused by moisture is seeable. In addition, it is probably the easier method to assess at first sight the size of a powder. Smaller powders tend to make more clumps.

Observing lines at the optical microscope

Apart from direct measures and tests on the binder or the powder, most information on lines and beds are obtained at the optical microscope. After a bed is printed, lines are still deep in the grooves, covered by the fallen powder.

The following aspects are part of the observations:

- type of bed;
- type of grooves;
- interaction between bed and lines during the extraction;
- quality of lines.

The extraction of lines

The extraction of lines is a difficult task, because they are very delicate. If raised on one side, they do not even support their own weight and crack; and when falling they continue to break in multiple parts. And also, they are often stuck to the surrounding powder. The typical technique to clean lines from the loose powder is using an air jet. The pressure is so low, that there is no reading on the gauge of the lower pressure compressed air circuit. A needle is used to concentrate the air jet, and the smallest available at the laboratory (pink) is used. In some cases, to further reduce the air pressure, a T-tube (Figure 33 of page 97) is connected with multiple needles, to obtain a lower optimal pressure.

Behavior of beds during the line extraction

The direct observation of beds is not able to provide useful information on how will be the quality of lines. On the opposite, the dynamic behavior of a bed, that is its behavior during the line cleaning and the powder removal, is directly correlated to the line quality. This is a proof of the correlation between line mobility and line quality.

Four main different bed types have been observed.

1. Alumina powders. They were most beds. Usually the best the lines, the easier the removal. This is true for the powder surrounding the lines. With good lines, there is a good separation. This does not necessarily means that all grains are free one another: they can also be in clusters.
2. Metal powders are about twice as dense than alumina, then they are heavier. They need a higher pressure and a larger needle (azure).
3. Slurries are the most compact. By this term I refer to a series of beds made trying to increase the powder density. They were made adding water to the powder bed and then drying before printing. Lines were almost impossible to extract. Air alone was not sufficient and a small painting brush in the direction of lines was used to separate grains before blowing. Lines were probably not even formed!
4. Firing is another cause for grains to stick to one another.

The Environmental Scanning Electron Microscopy (ESEM)

There are different types of SEM. The environmental SEM used in low pressure mode with water vapor, allows the observation of any type of material and does not require electric continuity between specimen and support, so also ceramic samples can be observed without gold or carbon plating.

The main advantages of the ESEM with respect to the optical microscope are: the higher magnification and the higher field of depth.

The ESEM is great for measurements and to observe any kind of detail at any resolution, allowing to save images.

Also the distribution of grains of different size or shape and their connections can be observed.

But nothing is perfect in this world, and here are its main drawbacks:

- The higher magnification is important to observe the minimum details of lines to understand the ongoing phenomena; but to assess the line quality, the magnification available on an optical microscope is sufficient. And also, the classification of defects provided in this paper is a powerful tool to assess the quality in a more objective way.
- Regarding the field of view, because almost everything is on focus, there is a sometimes the difficulty of assessing what is in front and what is back.

These are additional drawbacks for numerous routine experiments.

- Very **delicate samples** need to be transported outside and across buildings with any weather, installed on a different support and put inside the vacuum chamber of the microscope. The turbulence in the chamber is also a cause for spoiling samples, unless special measures are taken, like setting the support elevation at the minimum and moving the table on one side to avoid a direct destructive air jet from the scan beam.
- The **higher setup time**. Before the observation, it takes several minutes to do the vacuum. If the sample is not positioned well, it needs to be done again.

- It is always required that the specimen are **prepared** for the observation, so the use of an optical microscope for cleaning and extracting lines for observation is necessary anyway.
- Only observations in **static conditions** are possible, because in the microscope chamber there is vacuum. No air jet is possible, unless the specimen is extracted every time. Therefore, it is not possible to understand the interaction between lines and the bed. In addition, it can be considered a destructive test, in the sense that if the lines are extracted from the bed, no more information can be obtained beside those regarding the line itself.
- The image acquisition is very **slow**. The screen refresh at low scan rate, which means with better quality, takes several seconds, so looking around inside a sample takes hours. The highest scan rate is only sufficient to perceive the presence of strange elements, and after a lower scan rate is required. The image acquisition at good resolution takes several minutes.

Additional information on the ESEM available at the MIT can be found in Appendix E (page 120).

Conclusions on microscopes

The use of the ESEM was very time consuming, but it revealed much fundamental information on the process and it was a necessary instrument to proof most of the observed phenomena, at a magnification between 1000x and 3500x. The optical microscope is always necessary for the sample preparation. A 50x to 100x magnification is sufficient for the quality assessment and for routine debugging.

Chapter III.

THE HARDWARE CHARACTERISATION

Introduction

In this chapter, the main features of the used printhead along with the necessary tests to determine them are described.

The main principles of these technologies with all possible variations can be found in [Heinzl-Hertz85].

Developing a new thermal printhead is out of the scopes of this study, so a commercial one has been used for preliminary tests. Previous work [Baker97] was already carried out at the 3DP Lab using a HP printhead, model 51626A. Many useful information to operate it outside of a printer, that manufacturers usually do not provide, can be found there, such as wiring, input voltage and so on. The basic and additional specific information coming from tests that were necessary for the examined application are reported in this chapter and in appendix.

The main purposes of these tests are:

1. to retrieve quantitative data on the used printhead and
2. to determine which parameters are controllable.

Continuos Jet (CJ) and Drop on Demand (DoD)

CJ printheads are designed to emit a steady stream of tiny drops of ink. The drops are charged with static electricity and are then "steered" either onto the printing medium (power bed or paper) or into a recycling reservoir by charged fields. Today, commercial inkjet printers rely mainly on DoD technology, which produces single droplets when needed. There are two methods inkjets use to achieve this speedy spitting: thermal and piezoelectric.

Drop on demand versus continuous jet

3DP is a mature technology. Performance improvements are expected now from radical changes. Drop on demand can overcome several inherent limitations of CJ printing, which has been traditionally used since the beginning.

Some advantages are related to vector printing, which of course gives higher flexibility and which is shown to deliver better surface finish with a suitable path design.

The drop size is slightly smaller, so the nominal process resolution is. A better control over the drop size is also possible.

The drop speed, which affects the binder penetration into the powder bed, is about the same.

The drop frequency, which directly affects productivity, is instead lower, about two orders of magnitude.

They are comparatively inexpensive to produce and because of their simplicity they can be mounted close to each other to form a multinozzle array, whereby the speed becomes comparable to that of CJ systems.

Regarding the ability to change the frequency, which is desirable in vector printing, to support the speed change, drop on demand printhead are more flexible. A printhead is under development [Sachs00] based on the piezo technology that can operate between single and up to 3kHz. Commercial bubble jet printhead can operate up to 1.5 kHz.

Regarding the distance, they do not allow printing distances of more than a few millimetres between the printhead and the record receiving surface; continuous jet excel in the ability to print on surfaces as far as 2-3 cm from the printhead.

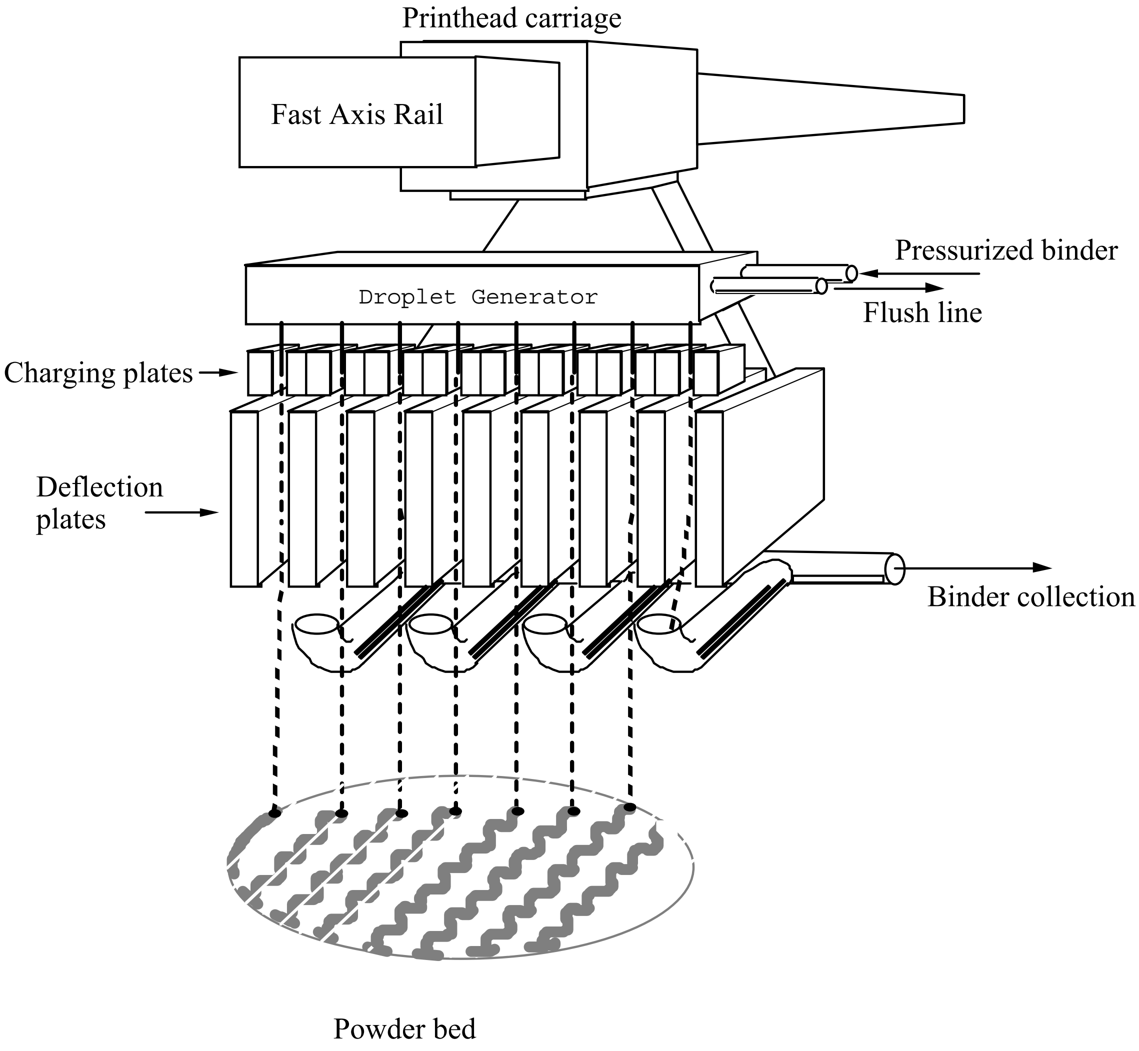
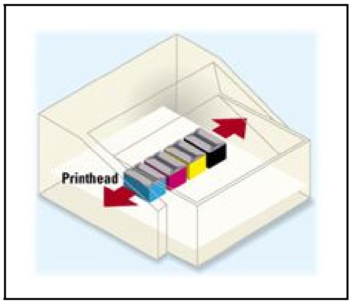


Figure 2 - Scheme of a Continuous Jet (CJ) printhead

The advantage of the continuous jet instead of the drop on demand is represented by the possibility to give to the stream a proportional deflection. Thanks to this deflection every nozzle is able to cover a space of 2 mm of the powder bed. This defection procedure is allowed by the combination of two different electric fields located in the printhead (Figure 2).

More on the comparison between raster and vector printing can also be found in [Sachs00].

DoD printing: thermal (or bubble) and piezo inkjet



Home and office inkjet printers either work by the thermal (bubble jet) or piezo principle. In the thermal inkjet print head, the actuator is in fact a heating plate which creates a steam bubble in the ink, which ejects a drop of ink through the nozzle (opening) onto the paper, in a direction either parallel (Canon) or perpendicular (HP) to the heating element. In the piezo inkjet head (Epson), the actuator is a piezoelectric element, i.e. a piece of material which deforms under the influence of an electric field, and thus squeezes the ink chamber to eject an ink drop. This happens at very high frequency, so thousands of drops can be ejected in one second. The principle is rather simple, but the details make the difference, and these are highly proprietary (e.g. European Patent Application No. 0588241 A2 or U.S. Patent No. 4597794).

Piezoelectric printheads can use ink that dries faster and pigments that might be damaged by the temperatures in a thermal head. Also, a piezoelectric printhead is built into the printer, so only the ink cartridge needs to be replaced. Thermal inkjets incorporate the jet nozzles into each ink cartridge, which can increase the cost of the cartridge and thus the cost per page (but their cost is also smaller than the piezo). The downside is that if a piezoelectric printhead is damaged or clogged, the printer must be repaired.

Thermal Printhead

A thermal printhead uses a tiny heater on each capillary tube (Figure 3.a) to heat ink rapidly to its boiling point, creating a tiny bubble of steam (Figure 3.b).

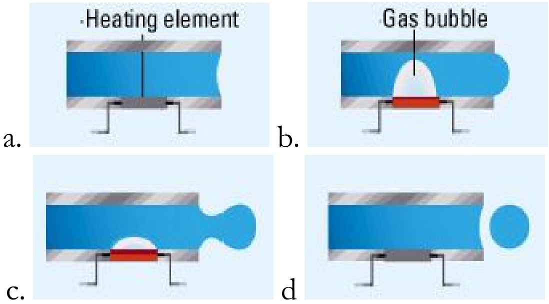


Figure 3 - Thermal printhead

This bubble forces a droplet of ink out of the end of the tube (Figure 3.c).

When the heat is turned off, the ink cools, and the tube is ready to be activated again (Figure 3.d).

Piezo Printhead

A piezoelectric printhead uses a special type of crystal that responds to electrical current (Figure 4.a).

Figure 4 - Piezoelectric printhead

When a charge is applied, such a crystal deforms slightly. In a printhead, the crystal's movement forces a tiny droplet of ink through a capillary tube (Figure 4.b).

When the current is removed, the crystal snaps back to its original position (Figure 4.c).

Printing ink on paper

Early personal inkjet printers produced droplets that contained about 86 picoliters of ink each. A picoliter is one-trillionth of a liter, which means that it would take roughly 11.6 billion of these drops to fill a liter bottle. Over the years, the technology has been refined, and now inkjet droplets each contain about 10 picoliters of ink -- 100 billion to the liter.

These tiny droplets create marks that are about 50 to 60 microns (one-millionth of a meter) in diameter, less than the diameter of a typical human hair. The smallest-size dot that the unaided human eye can see is about 30 microns across, so these dots are approaching the limits of our perception.

The incredibly small size of these droplets makes it possible to increase the resolution of the printed output. It takes about a 35-micron dot to create an output of 720 dpi, so these drops overlap slightly at that resolution. There is more to print quality than simply resolution; other factors play important roles in how we perceive the detail in a printed image. Some printers control the shades and intensity of colors by layering up to 16 droplets in the same space. This increases the number of colors created, improves anti-aliasing (getting rid of "jaggies"), and makes smoother transitions from one color to the next.

Table II - Physical and chemical properties for the HP51626A printhead [HP99]

Appearance: black liquid	**Physical state**: liquid at room temperature
pH: 8.3-8.7	**Solvent content**: <10%
Solubility in water: soluble	**Vapour density**: >1 (air = 1.0)
Odour: not applicable	**Vapour pressure**: not applicable

Table III - Ink composition for the HP51626A printhead [HP99]

Component	**CAS No.**	**% by weight**
Trade secret colorants	not specified	<5
2-pyrrolidone	616-45-5	<10
Trade secret organic materials	not specified	<5
Water	7732-18-5	balance

The liquids printed

The first tests of the printhead have been performed using a brand new one containing ink. Many different patterns have been printed changing the drop frequency and the speed of the slow and the fast axes (Figure 6). Next, the ink has been replaced with water considering that the binder used is a water solution. Both ink and water have been printed on paper and powder. The HP51626A Ink contains some amount of ethylene that has a small sticking ability. With both ink and water, the printed lines are clearly visible in the bed, but they are very inconsistent and a small vibration makes them disappear. In the case of ink, after a small vibration, grains remain black and are mixed with white powder. To make the ink disappear too it is enough to heat it over 400° C.

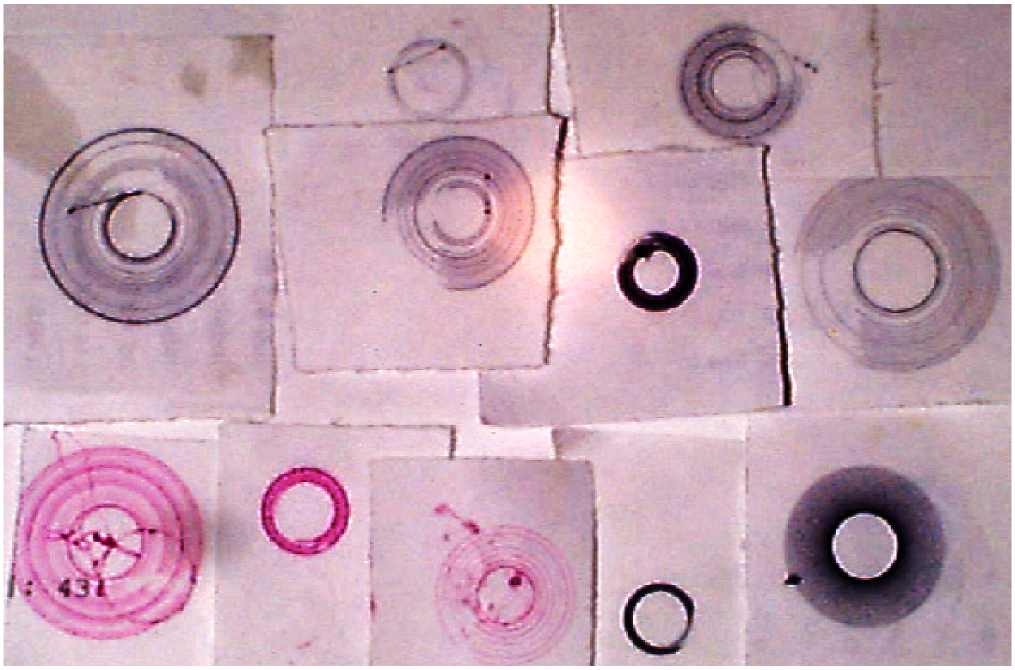


Figure 5 - More patterns printed on paper with standard ink (black) and a 50% vol. water solution of colloidal silica in ethylene glycol with (pink) food color

General information

The used printhead is based on the drop on demand technology. DoD inkjet methods include: thermal or bubble jet and piezo. The main principles of these technologies with all possible variations can be found in [Heinzl-Hertz85].

A huge amount of investments has been devolved in the development of printhead cartridges. Their production cost is relatively low thanks to the very large-scale economies, but their price is kept high and provides important income to the few world producers. As a market strategy, printers, who are high tech products, are sold below cost at affordable prices and most of the total printing cost is charged to printheads.

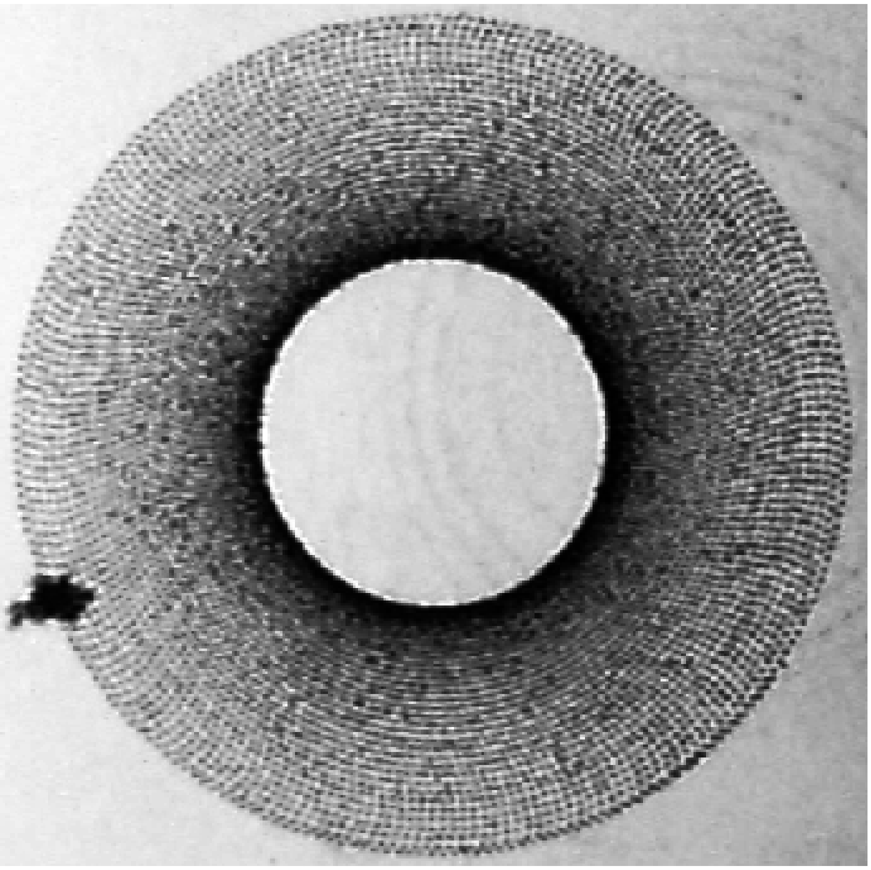


Figure 6 - An example of pattern printed with ink on paper

Among the main world printer manufacturers, HP and Canon use thermal inkjet on their printers, Siemens and Epson use piezo printheads.

In Appendix A a compatibility chart is available with the HP printer models using the HP 51626A cartridge.

Changing the binder composition

50% of CSEG is probably the lower limit under the constraint of structural resistance during casting. However, this does not represent a problem, because only a minimum structural resistance to remove the excess powder is necessary and after a post-dip is possible to increase it.

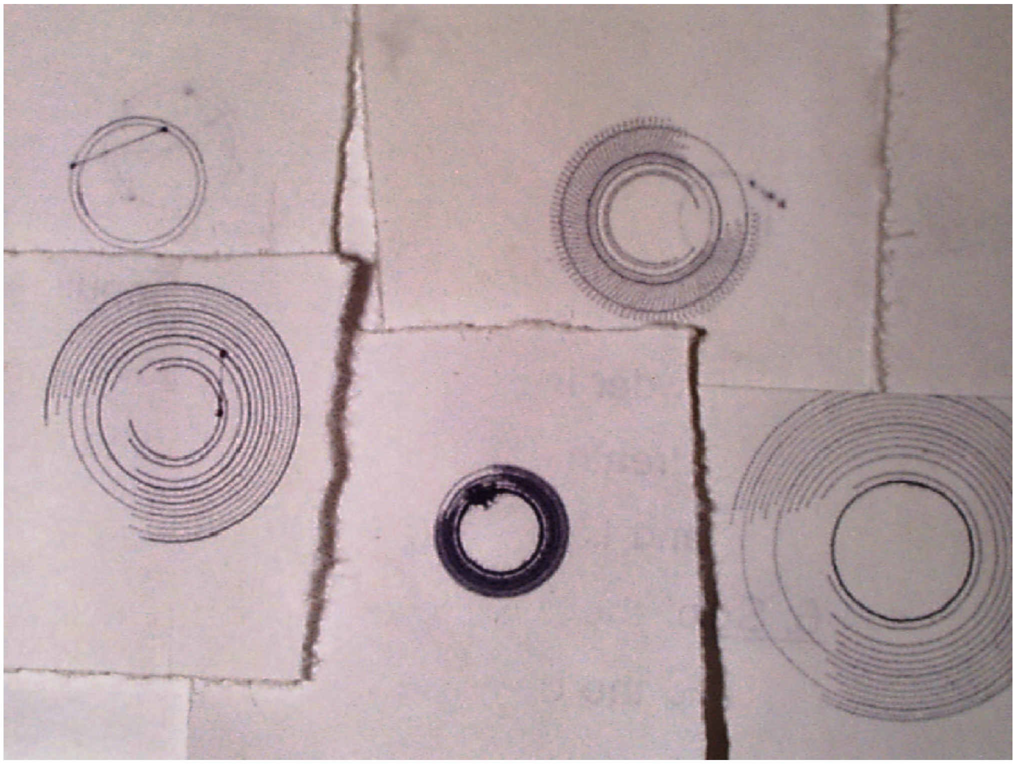


Figure 7 - More patterns printed on paper with standard ink (black). An example of set-up of the slow axis

The printhead characterization

<u>*Measuring the drop speed: the step method*</u>

Extrapolation from the flow rate

The drop speed can be extrapolated measuring the flow rate and the nozzle section [Curodeau95].

The droplet observation station

To accurately determine the drop speed and to observe other effects related to drop formation and flight, a device developed at the 3DP Lab is generally used [Chijioke98]. It is based on a camera taking consecutive frames with changing delays with respect to the generation of the signal that produces a drop. A monochrome camera is displaced with respect to the printhead in order to observe one drop in the centre of the image. Observing drops in the same position eliminates all the distortion effects problems. This requires an accurate relative positioning between the camera and the printhead, in addition to the wiring problems to get the sync input. The long set-up times, particularly for a different printhead (the station is designed for the CJ nozzles of the Alpha Machine), suggested finding a new faster method for determining the drop speed.

The droplet impact station was not used because the station needed some modifications, every set-up takes too long, a very accurate estimation was not necessary, and a (portable) method to be used on the developed machine was preferred.

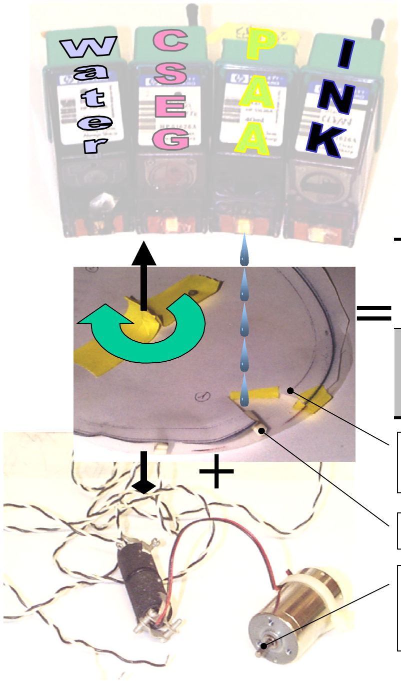
The developed method

At this stage an error of 10% or even more was enough. The following fast method has been developed. A disc is rotating at very high speed. A step of known height is applied on the disc. After exposing the rotating disc under the printhead for a certain time, a circle of drops can be observed. This circle is interrupted immediately after the step for the shading effect. The distance between the first drop after the step is directly proportional to the step height and inversely proportional to the velocity. By this simple relation, a good estimation of the drop speed was achieved. A scheme is displayed in Figure 8.

Implementation problems

The exact shade length should be measured between the point on the disc corresponding to the last point on the step edge and the center of the first drop. This can be easily performed with an optical microscope as the one available at the 3DP Lab, because it is possible to focus points at different height while measuring in the *horizontal* direction (because the focus intentionally only affects the vertical axis). The micrometric displacement of the microscope X-Y table has been used to determine the distance. The drop center is instead a theoretical point, so the first drop point has been considered and the distance has been after corrected by adding half of the drop size (which was previously measured on the same printed medium).

It can be observed that a drop hitting the edge step is scattered in multiple smaller droplets with unknown direction. It is however very unsuitable that their vertical speed increases. To minimize the scattering effect an *absorbing* material has been used for the step.



CSEG: Colloidal Silica in Ethylene Glycol diluted 1:1 (vol.) in water

INK w/respect to CSEG: same density, lower viscosity (20-40% Ethylene Glycol with water)

PAA: Poly Acrylic Acid diluted 1:10 (vol.) in water

Comparative tests. Effects on the Drop Speed [m/s] of:	High Frequency CSEG 1 kHz	Low Frequency CSEG 230 Hz	High Frequency INK 1 kHz *16 Volt
High Voltage 17 Volt	15.5	15.3	12.5*
Low Voltage 14 Volt	11.8	11.4	-

First drop of circle of known radius

Step of known height

High speed motor rotating spindle at 4000 RPM

Drop diameter
17 Volt - 1kHz

INK: 55 µm

CSEG: 65 µm

Figure 8 - The step method to estimate the drop speed

Regarding the number of drops to print, it has been noticed that it is better to print two or three times the number of drops required to print a circle of touching drops. It could look better having separate visible drop, but the presence of empty spaces is critical for the measurement of the shade length, because there is no evidence that the first drop is the first possible drop. It has been observed instead that printing many overlapped drops yields a contrasted line with a well-defined first drop. This is particularly important when printing at low frequency, because the disc turns many more times before the necessary drop number has been printed and their distribution on the disc looks more irregular than printing at higher speed for a shorter time.

With the developed set-up, which will be described in a later chapter, it is possible to print a given number of drops. This eliminates the problems of synchronization with the disc rotation (it is enough to calculate an *integer* multiple of the number of touching drops to make a complete circle) and allows a higher repeatability between tests.

To achieve the required spindle speed a special 24 Volt motor has been used. Its maximum speed is over 6000 rpm, but because of the drag effects on the disc, the maximum achieved speed has been about 4000 rpm. The actual speed has been measured using a strobe light. The disc has been made with a standard sheet of paper cut to make a circle that became more rigid for the centrifugal force. To minimize vibrations, steps were positioned symmetrically on the disc. In the very first version developed in 8 minutes by prof. Sachs, a common plastic tape was fold up in two, but it was too soft to measure its height, and for this reason it has been replaced in further test. In this preliminary test, the measured drop speed of ink on paper, at 1 kHz has been 9.6 m/s.

To measure the drop speed on the 1:1 volume solution of Colloidal Silica in Ethylene Glycol and water another light printing medium was necessary. The examined solution is invisible on paper. It can be seen instead on transparency film as an opaque circle. This is also a more rigid medium. To minimize the drag a maximum of two steps were used. They were made of foam tape, 1 mm thick, coupled to get a 2 mm step. To further reduce drag, a sheet of paper is added that makes the transition to the step smoother. On the sheet of paper, two windows are cut to allow multiple uses of the transparency film disc. After one test, a new couple of steps is added to the disc and the paper cover is rotated to discover an other area of the film disc to print on. After measurement, the previous couple of steps can be removed to reduce the disc weight and drag.

Considering that the method is not very accurate, it has been mainly used in *comparative* test, e.g. performing couples of tests on lines printed close to each other. In particular, it has been used

- to compare and measure the drop speed of ink and of the mentioned solution, and
- to estimate the drop speed changes as a function of the frequency, and
- to estimate the drop speed changes as a function of the voltage.

The more difficult and also critical measure is the step height, of course if we consider that the whole analysis takes less than one hour for the set-up and about two hours for the tests described later. It has been simply made by carefully using a micrometer.

Results

The speed of the colloidal silica in ethylene glycol and water is 12.5 m/s.

The frequency affects the drop speed in the following way: a lower frequency gives a lower speed with a reduction between 5 and 20%.

The drop size

It has been roughly measured by weighing. A test tube, with a small opening to minimize evaporation, has been placed on a micrometry balance close and below the printhead. The weight value has been read at intervals of 5 minutes for 30 minutes tests. The test has been repeated for both ink and for the 1:1 volume solution of colloidal silica in ethylene glycol and water.

The drop frequency

Tests have shown that the HP 51626A printhead can be used at a frequency between 0 (single drops can be printed) and 1.5 kHz. The developed device operates continuously up to 1.35 kHz, for software limitations. The printhead can operate at higher frequency (it was tested up to 3 kHz) but after few minutes the resistor is burned so a standard use is not possible.

The HP 51626A printhead operates over 13 Volt. It has been tested up to 18.5 Volt in continuous use. The voltage affects the drop size, but not the drop speed. The drop formation process can explain this.

Applying a certain voltage heats the nozzle resistor, which generates a bubble of vapor around it. A higher voltage only implies a longer heating time and not a higher temperature, which instead remains constant. Consequently, the bubble increase produces the output of more liquid out of the nozzle orifice before the resistor cooling, the bubble contraction and the drop formation. The heating and cooling time do not change, so the drop speed is not affected by the voltage change.

On the opposite, a higher frequency yields a higher drop speed, for a kind of resonation effect.

There is probably a warm-up phase before the printhead is operating fully, which is relevant at low frequency (10 - 50 Hz). It has been observed that the resistance is not constant. It periodically rises and then goes down. The effect on the binder flow has not been investigated.

Using the printhead

Cleaning the printhead

With all the binders tested, ink, colloidal silica in ethylene glycol (CSEG), Poly Acrilic Acid (PAA) and of course water, clogging is not a problem. If left to the open air, nozzles will clog in 2 or 3 days. If covered with a paraffin tape, which keeps them humid, they last over a month.

To clean nozzles, after filling the printhead with distilled water, the first thing to try is just using a soft cotton wool ribbon with distilled water, to avoid deposits. If this is not sufficient, the further step is using a sonicator[3], putting the printhead in a glass of water and submerging the nozzles, again with clean distilled water. This method was used also with printheads left abandoned without protection for an unknown time and with an

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[3] Available in the main lab.

unknown dry binder in, just increasing the cleaning time. Blowing through the upper printhead hole also helps.

To rapidly check if the binder is coming through, absorbing paper is a good medium to collect ink, because it does not spills: ink can also be harmful if it touches the skin. If the binder is colored (ink or with food colors added), it is easier to see.

For different binders, like water, colloidal silica in ethylene glycol or polyacrylic acid that are transparent, a clean glass surface is preferred, because they are hard to see when printed on paper.

In addition, if the glass (or the paper) is moved fast below the printhead, an immediate qualitative assessment of the regularity of the drop size and frequency is available.

Always avoid to scratch the nozzle surface or to touch it.

Please note that if a nozzle is operated for a few seconds while it is clogged, it can be irreversibly damaged, because the resistor will heat too much and burn. The resistor heating can be observed as an increase of resistance.

Debugging nozzles

The best way to monitor the state of the electronic part of a nozzle is to connect a tester in parallel and check the resistance value. When printing, the very short duration (2.5 μs) of the current impulses does not affect the measure. The nominal value is about 30 - 34 Ohm. A possible reason for the incorrect reading of the resistance is the presence of humidity or of some binder between the printhead support and the electrical contacts. In this case, it only needs drying with some soft paper. Another reason can be the incorrect positioning of the printhead and consequently a bad contact. To avoid this, when installing it, first push the printhead inclined towards the bottom of the support and then secure it with the spring.

When printing, the nozzle resistor heats and increases its resistance. 220 Ohm have been reached continuously printing lines in series of half a minute at 18.5 Volt and 1.5 kHz. This is probably the upper limit before burning, and it can be safely reached in any combination of voltage and frequency, although specific tests have not been carried out.

For reasons that have not been investigated, using the Tektronic CFG250 wave generator in preliminary tests, nozzles burned when switching frequencies up or down by multiples of 10 with the available control. This low flexibility of the first equipment was also a reason for upgrading to a PC controlled printhead. To avoid the problem mentioned, the printhead output should be turned off with the switch available on the feeding circuit.

Connecting multiple nozzles (to a single circuit)

One single electronic circuit is able to drive up to three nozzles connected in parallel. Of course they all will print identical patterns. With more nozzles, the current is not enough to generate drops. The 52 nozzles available on a printhead are distributed on two parallel rows of 26 each, which use to be parallel to the slow axis. To simultaneously use two or three nozzles to print the same line, they should be selected on the same row using the slow axis as the fast axis. Or up to two nozzles on two different rows can be used to print one line using the fast axis. And so on with all possible combinations. An immediate application of this is the multi-pass method described later in this report.

With small modification to the present set-up, it would be possible to drive many nozzles simultaneously with different patterns. About 20 can be used using only one parallel port (like in the present hardware configuration) and 20 more for each added port controlled by the software. 20 or more electronic circuits identical to the one used, which converts the square wave into pulses and amplifies the signal from 5 to 13 - 18 Volts, should be build. The rest is state of the art.

Conclusions on the printhead characterization

Drops of colloidal silica in ethylene glycol are larger and faster than ink drops.

HP datasheets are enclosed in Appendix A, page 1 for a comparison between the composition, density and viscosity of black ink and the water solution of colloidal silica in ethylene glycol.

Chapter IV.

THE MATERIAL SYSTEM CHARACTERIZATION

This chapter deals with the main information that can be extracted form the material system. These information are available **before** printing, so they can be used in two ways:

1. to predict the process performance once a correlation has been established;
2. to check the status of the process parameters related to the material system and to correct them.

The kinds of information available before printing concern:

- the binder,
- the powder alone, and
- the power bed.

Of course the powder bed is an expression of the powder behavior, but it is relevant for the process as a whole.

The binder

The main properties of the binder are as important for the process as the powder properties are. They can be changed by varying its composition: in this particular case the type of colloidal silica in ethylene glycol and its percentage in the water solution. No tests have been performed on these aspects and the standard composition has been used in all experiments.

Powder variables

The following information can be used to characterize the behavior of powders. For each of them the following information are provided: definition (what), purpose (why), method (how), and other features.

The powder density

It depends on the packing. The apparent density corresponds to simply pouring the powder. The tapping density is achieved with high intensity vibrations at different frequencies. The used device is a powder container on a sliding guide vertically raised (by a cam rotating at different spins) and dropping.

Measuring the powder mobility

The main method to assess the powder mobility is measuring the angle of repose of a cone of powder, obtained pouring it from a small hole not too high with respect to the cone vertex (to reduce the impact effects). The larger the cone, the more accurate the measurement, however, considering the usual amounts to make one powder bed, cones of 2 - 3 grams of powder have been made. The typical height of the cones was about 10 mm. Considering the small dimensions, the measurement have been performed using a pre-setting machine which is available in the workshop of the department.

The main problem with the measurement is that in most cases the slope is not straight, so it can have locally different angles. In some cases, as indicated, the angle is constant. This is also an indication that the powder has a more regular behavior. And also the cone can have slope changes on the different sizes. The following criterion has been assumed: taking the maximum and the minimum average angle with respect to the ideal vertex, rotating the cone. By moving the cone, the powder rearranges, yielding lower incorrect angles. To avoid this, the measurements are considered valid until the top of the cone does not lower.

Table IV - Apparent and tap density of the tested powder mixtures

Powder	*App. density [g/mm³]*	*App. density [%]*	*Tap density [g/mm³]*	*Tap. density [%]*	*Remarks*
SS 316L					
SS 316L					(*)
Al 20 + <10	1.76	43	2.47	61	2 : 1
Al 20 + <10	1.61	40	2.32	58	1 : 1
Al 20 + <10	1.77	44	2.22	55	1 : 2
Al 20					Coated with 0.3 % DarvanC
Al 20					Coated with 7 % DarvanC
Al 20					+ 20% <5 μm
Al 20					+ 12% 5 μm equiax
Al 30					

The difference between the apparent and tapped powder density is also an indirect indication of the powder mobility.

The angle of repose

Definition: It is the angle formed by a cone obtained by pouring the powder from point (through a hole). The height of the hole from the base should not be greater than 1/3 of the final cone height. A greater amount of powder yields a more accurate

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(*) The above after ball milling, coating, and decanting of suspension [Baker97].

measure. 1 - 2 grams of powders have been used during tests making cones of about 10 mm.

Purpose: The way the powder rearranges in the absence of vibrations is an indication of the flowability in semi-static conditions.

Method: The angle can be measured in the following two ways, among others:

1. by measuring the cone base area from a top view and the cone height. This method has the uncertainty of determining the cone vertex but it has the advantage of giving an average of the different slopes;
2. by measuring the average angle of the cone profile or by measuring the width and height from a side view of the cone. This method only requires one view and it has been used. The cone profile has been projected with a pre-setting machine[4], and it is rotated to perform measures from different views. The range of angles is given by the maximum and the minimum measures. The test becomes invalid if/when the cone vertex gets lower for vibrations during rotation.

Features: This measurement is not very accurate because grains tend to stick and give irregular profiles or different slopes. The uncertainty varies between ±1° and ±5°. The angle of repose uncertainty is also a useful information about the powder behaviour.

The presence of clumps may make the profile very irregular with high local maxima and minima, which make the test less reliable. The angle of repose of powders is measured in the same condition of printing.

The minimum range of variability of the angle of repose (not indicated in the table) is ± 1°. An asterisk * indicated the presence of clumps.

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[4] The machine used is located in the LMP workshop of the MIT at the first floor (bldg. 35). When using alumina powders on machine tools special care should be paid to avoid spills on the tables, because it is harder than metals and may cause wear and gripping.

Table V - The angle of repose of the tested powder mixtures at room temperature and after heating

Powder	***Room Temp.***	***Hot (80° C)***	***Remarks***
SS 316L	65	45*	
SS 316L	48.5	25	(*)
Al 20	37.5 ± 1.5	23.5 ± 1.5	
Al 20	38 ± 2	32 ± 2	Coated with 0.3 % DarvanC
Al 20	38 ± 2		Coated with 7 % DarvanC
Al 20	52	53	+ 20% <5 μm
Al 20	50	49	+ 12% 5 μm equiax
Al 30	41 ± 3		

Because of the low wettability the stainless steel and those coming from coating, heating allows reducing the presence of moisture and consequently the angle of repose. The same effect is obtained on coated and uncoated pure alumina. The elimination of the smallest grains (≤ 1 μm) and ball milling strongly reduced the angle of repose for the stainless steel [Baker97].

The presence of DarvanC, which is a polymer coating, slightly increases friction.

In the case of alumina, the presence of small grains produces clumps that remain in the bed also after heating and reduce flowability.

Conclusions on the angle of repose

The main problem with the measurement is that in most cases the slope is not straight, so it can have locally different angles. In some cases, as indicated, the angle is constant. This is also an indication that the powder has a more regular behaviour. And also the cone can have slope changes on the different sizes. The following criterion has been assumed: taking the maximum and the minimum average angle with respect to the ideal vertex, rotating the cone. By moving the cone, the powder rearranges, yielding lower incorrect angles. To avoid this, the measurements are considered valid until the top of the cone does not lower.

A better test than the angle of repose would be exploiting the principle of the hourglass: measuring the time a certain amount of powder takes to flow through a predefined hole. More work needs to be done on this.

The difference between the apparent and tapped powder density is also an indirect indication of the powder mobility.

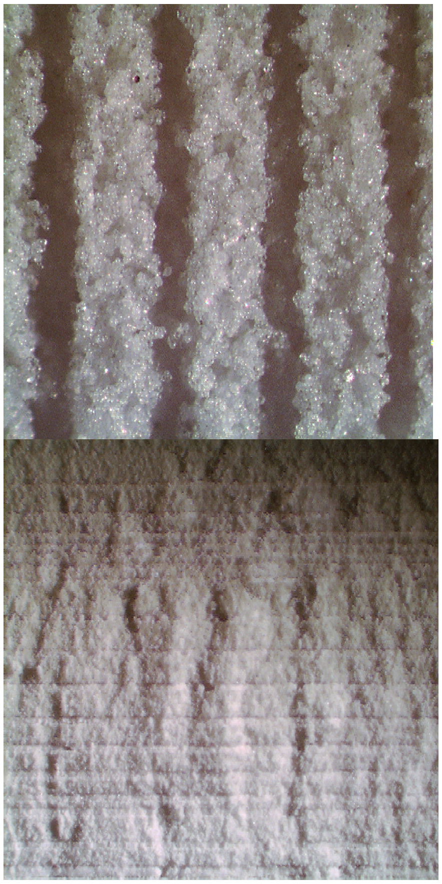


Figure 9 - Beds containing low quality lines (top) and the best obtained ones (bottom).

The quality of beds before printing

A correlation between the bed aspect and the quality of lines was not found. This means that the observation of a bed does not allow predicting the line quality.

Here are some limit examples. The lines contained in the bed in Figure 9 top are of low quality because the presence of the surfactant Duramax produced sticking, so they are full of clumps. The bed displayed on the bottom is instead very irregular, but grains have are free from each other.

An estimation of the powder bed density from the line depth

A rough estimation of the powder bed density can be obtained by measuring the empty volume of a groove and the volume of the line. These measures can be done in the simplest case with an optical microscope. The main problems with these measures are the view angle (usually from top, because the powder bed is disturbed if it is inclined and microscopes usually have a vertical axis) and the absence of objective references (like the bed or the line surface). To overcome both problems, the best way to take measures is to use grains as units. Of course this is possible only if their size is know and fixed, e.g. if they are spherical, regular and with a narrow size distribution.

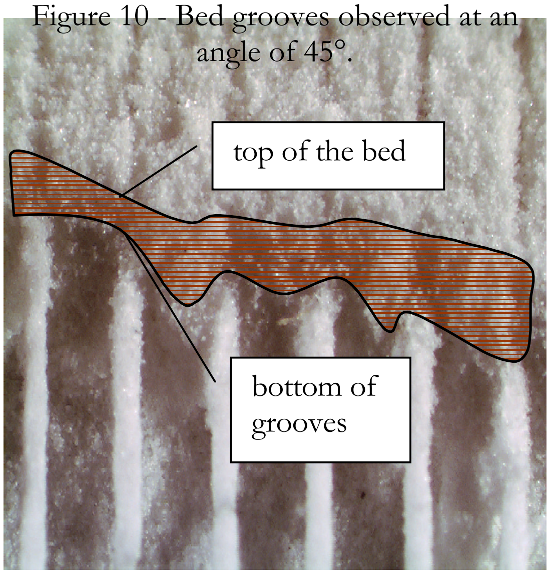


Figure 10 - Bed grooves observed at an angle of 45°.

In Figure 10, a view of the grooves is shown. After calibrating the image resolution (in this case 2 pixel/μm) the groove depth can be estimated.

The simple hypothesis behind this estimation is that the line is formed with all the powder formerly contained in the groove. The increased groove diameter due to the compression of the powder below the line due to its weight is neglected, so for metal powders that are heavier, the estimation is less accurate than for alumina powders. Lines are usually cylindrical and their average diameter and section are easy to measure.

The density of the line is assumed equal to the tapping density and should be measured with a specific test.

This technique cannot be used to obtain a quantitative estimation, but it is useful in comparative terms: the deeper the line, the higher the difference between apparent and compressed density or simply the lower the power bed density.

After performing many experiments, one get a feeling of this estimation of the apparent power bed density by direct observation, So also before measurements, one can have an idea of what is going on.

This estimation can be improved adding further hypotheses, for instance by considering the amount of binder printed for unit of length, but this goes behind the main purpose of this method.

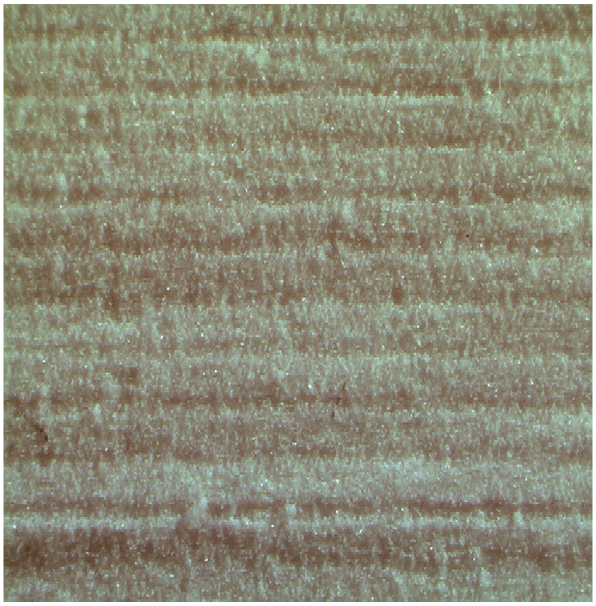


Figure 11 - A bed of 20 μm spherical alumina powder with lines spaced 500 μm almost completely covered by loose powder

Information on lines

The density of lines

An estimation of the line density can be achieved in two different ways exploiting the same principle: by measuring the primitive ball or line volume and subtracting the volume of voids, assuming it is filled with the binder.

In the first case, it is enough to measure the diameter of the primitive ball, assuming it is spherical. The volume of voids corresponds to the printed drop volume.

In the case of lines, they are assumed as cylindrical and their diameter should be measured. The average volume of voids for unit of length is given by the drop volume divided by the drop spacing.

So the density of lines estimated as the primitive ball or line density is

$\rho_{ball} = V_{drop} / V_{ball}$

$\rho_{line} = V_{drop} / (D_s * V_{line})$

with the conventions indicated.

Chapter V.

THE EXPERIMENTAL SET-UP

The main benefit of the developed set-up is to allow the user changing many different parameters in a single test and to save all their numeric values in a detailed report. This benefit is very important for the following reasons:

1. because it reduces the number and time necessary for experiment;
2. because it allows making comparative tests on the same power bed, and all power beds are unique, so it is very important to change all the other parameters as much as possible;
3. also observations are easier, with all samples in a single place, that can be compared to each other, are easier to store, and less waste of powder.

Lines versus rings

The main advantage of making a ring machine is that it has a table mounted on a motor as the fast axis, instead of a linear guide. A rotary table is also usually less expensive and easier to assemble.

Another advantage is that the speed changes proportionally to the radius, allowing variability during tests.

The same happens with the slow axis regarding the line spacing, unless the slow axis is set perpendicular to the fast axis and aligned with the centre of the rotary table. If it is not, there is a geometrical amplification of the spacing, allowing a higher accuracy. However a software correction is necessary.

On the opposite, printing lines instead of rings has the following advantages:

- beds are exploited better, as the entire surface can be filled with lines;

- lines are easier to remove and observe in the bed, and they also have all the same length;
- line spacing is constant and requires a less accurate positioning of the two axes at the machine set-up.

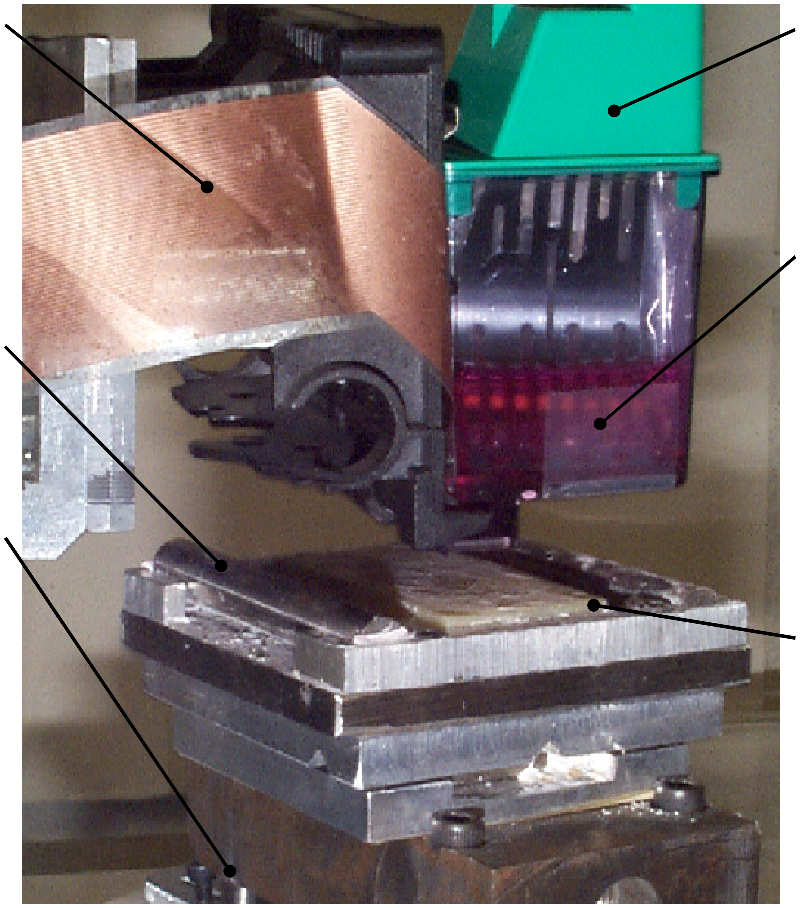
Benefits and drawback of the two configurations are summarized in Table VI.

Table VI - Comparison between the ring and the line machine configurations

Feature	***Ring*** ↺	***Line*** ⇉	***Preferred***
Machine set-up	easier assembly	higher cost	↺
Alignment of the two axes	accurate positioning required	not required	⇉
Line spacing	accuracy can be increased with axis displacement	easier control, no software correction required	
Fast axis speed	extended range	better control	
Powder bed and specimen	worst powder exploitation	easier line extraction and observation	⇉

The 3DRing machine

A scheme of the main functional parts of the 3DRing machine is displayed in Figure 12.



The control

A PC driving an external electronic circuit generates a series of pulses to print drops at a given frequency.

Stackable shims

allow spreading beds of different thickness.

The rotating platform

with a switch connected to the PC to measure the actual speed and all the consequent process parameters.

The printhead

A Drop on Demand, bubble-jet commercial printhead.

The binder

Colloidal Silica in Ethylene Glycol in water, with food colour to enhance the contrast of lines within the white Alumina powder bed.

The power bed

Laying on a detachable support, which allows an accurate repositioning.

Figure 12 - The experimental set-up

To easily re-position the bed on the moving fast axis, below the printhead, an interface made of two plates has been used. The upper one has two perpendicular triangular section grooves that match three spheres stuck in the lower plate: one groove matches one sphere, the other groove, matches the other two.

In fact, an accurate relative bed-printhead positioning was not necessary, as all the lines have been observed separately to each other and have printed sufficiently apart (usually between 40 and 50 um). Nevertheless, a fast positioning system was necessary when printing on the same bed in different conditions, for instance at different temperature.

The table spin for the ring machine and the translation speed for the line machine are manually selected, but they are acquired and saved in the report by the PC through a switch.

Low speed tests

The 3DRing machine gave some vibration problems at low speed, below 20 rpm. Considering that the nominal speed of the used motor was 64 rpm, the motion became very irregular because of the bad behavior of the magnets. This was the main reason to switch to the 3DLine configuration.

For lower speeds, on the 3DRing machine, low speed tests were only possible using the slow axis as the fast axis and manually moving the power bed after each line.

In the line configuration of the machine, a new controller, model 838 from Bodine Electric Company, has been used to extend the operative range at low speed (0.7 mm/s) and to continue to operate at normal speed (10 mm/s).

The 3DLine machine power and some strange interference problems…

To achieve the highest speed, the 120 Volt DC motor has been fed with three power supply in series, one 26 Volt and two 60 Volt. For still unknown reasons, when powering on any of the power supply, a nozzle was burned! Using the new controller or gradually increasing the voltage using the powers supply knob avoided this problem. It should be noticed that the power supply of the machine and the printhead circuit are completely separated and they only have in common the main net power. All the machine parts have been grounded. The more suitable hypothesis was that the high start-up current required by the motor, interfered with the main power and that very high frequency spikes from the feeding circuit of the printhead burned it. With the oscilloscope connected to the nozzle, several random signal oscillations have been occasionally noticed within the 2.5 μs pulse that produces a drop. The voltage was sometimes higher than the nominal voltage.

Chapter VI.

THE CONTROL SOFTWARE

The drop frequency and the line spacing are controlled by the PC. All the parameters are saved in a report. This allows a high flexibility in the process parameters selection. Considering the support size and the slow and the fast axis operative range, a single bed contains 30 primitive rings or lines at a spacing of 500 μm and up to 100 with a lower spacing, with different parameters each, allowing a direct comparison with the same bed conditions.

The main benefit of the control software is to store all the necessary information of each test. The report produced are a support for the direct observation.

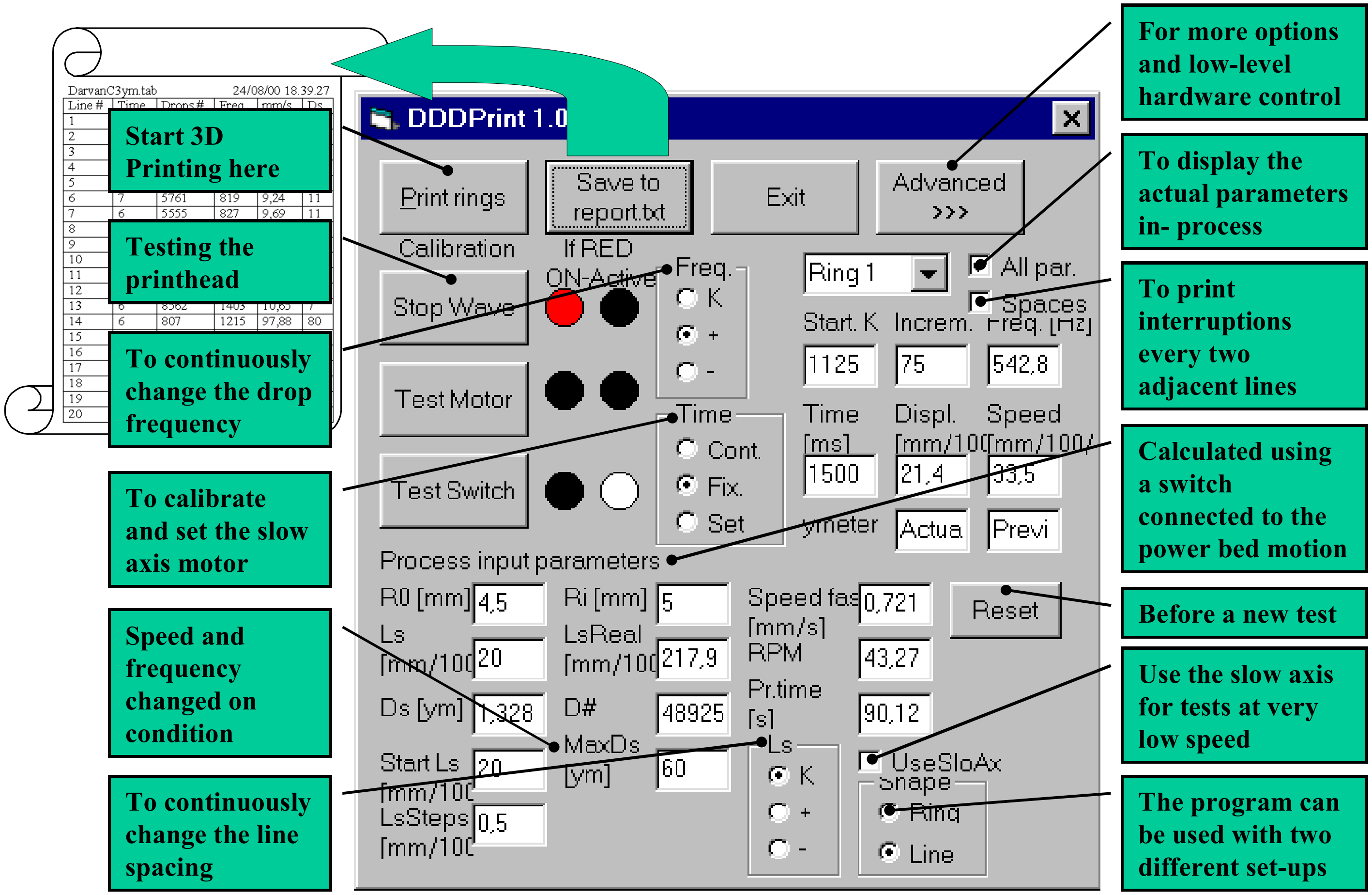
The software also allows printing particular patterns.

To assess the effect of line mating, the line spacing can be continuously increased or decreased by a predefined step. It is also possible to add line interruptions at predefined intervals to assess the line quality only on odd or even lines.

Lines can be printed one or more times.

In Figure 13 the main window of the program interface is displayed with the available settings. The program has been developed with M$ Visual Basic 5.0.

The last version of the software compiled with all the sources has been delivered in digital format, with the usual methods.



Freq.: ○ K ● + ○ -

Time: ○ Cont. ● Fix. ○ Set

Ring 1

☑ All par.

☑ Spaces

Start. K: 1125

Increm.: 75

Freq. [Hz]: 542,8

Time [ms]: 1500

Displ. [mm/100]: 21,4

Speed [mm/100/: 33,5

ymeter: Actua | Previ

Process input parameters

R0 [mm]: 4,5

Ri [mm]: 5

Speed fas [mm/s]: 0,721

Ls [mm/100: 20

LsReal [mm/100: 217,9

RPM: 43,27

Ds [ym]: 1,328

D#: 48925

Pr.time [s]: 90,12

Start Ls [mm/100: 20

MaxDs [ym]: 60

LsSteps [mm/100: 0,5

Ls: ● K ○ + ○ -

☐ UseSloAx

Shape: ○ Ring ● Line

Start 3D Printing here

Testing the printhead

To continuously change the drop frequency

To calibrate and set the slow axis motor

Speed and frequency changed on condition

To continuously change the line spacing

For more options and low-level hardware control

To display the actual parameters in- process

To print interruptions every two adjacent lines

Calculated using a switch connected to the power bed motion

Before a new test

Use the slow axis for tests at very low speed

The program can be used with two different set-ups

Figure 13 - The control software

Chapter VII.

LOOKING FOR THE PERFECT LINE

Introduction

As in many other projects, the main purpose of this one is the process optimization, in particular focusing on the surface finish. But instead of going through to the fabrication of a whole part for a certain application, with a given material system, and finding the necessary parameters, all the resources have been invested to understanding the line formation phenomena. Therefore, 50% of the work is on the optimization of lines, and 50% is a detailed interpretation of this basic process.

The formation of good quality lines is a necessary step for the process optimization, to achieve good mechanical resistance, better surface finish and geometrical tolerances. In this chapter, a definition of line quality is provided and the main parameters and variables to improve it have been pointed out.

The quality of lines?

Judging the quality of a line is a subjective task, unless objective criteria are defined.

Only the visible features are relevant to this study, because the structural issues are a direct consequence of a regular and compact powder-binder distribution, or anyway, post-processing would allow achieving the required mechanical resistance.

In [Bredt95] the following parameters were used: the visible area of the line, divided by its length, after binarization at 16 gray levels.

A good absolute method is to take measures of the lines printed, which requires the development of image processing algorithms. Pictures can be obtained from an optical microscope or a SEM. The main problem of the former is the low field depth that does not yield a good general view of a line and it does not allow a good estimation in the case of small differences. The main problem with the latter is longer time required for the preparation and observation of the specimens. A discussion on additional differences is provided later in this chapter. A problem of this method is that only geometric features could be extracted from the line images and an analysis of other aspects, e.g. the powder configuration, would require additional observations.

The theoretical roughness of a line

We calculate here the surface finish of the mould, assuming that it is the same as the line. In fact, this value represents the upper bound, because the primary surface texture of the final part depends on the lines and the layers mating and on the particular printing techniques used. Special methods are available to reduce it.

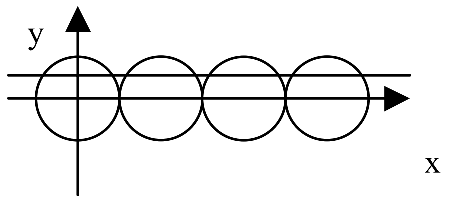


Figure 14 - The theoretical roughness of lines

The cast metal parts roughness will be generally lower than the ceramic mould one, and it depends on their castability [German94]: the less castable they are the lower the surface finish of the final part.

The best theoretical surface finish in term of the standard parameter Average Arithmetic Roughness R_a in the case of a powder with a perfect distribution of grain of the same size (Figure 14) is

$$R_a = 1/L \int |y| dx$$

for 20 μm grains, the minimum theoretical value can be easily calculated. A rough estimation is a quarter of the grain size.

$R_a \approx 5$

The addition of small particles, by filling the external voids could drop it down to 1.

A more accurate estimation of the on theoretical R_a on perfect lines (cylinders) made of spheres is also possible with easiy geometrical considerations.

The theoretical spatial distribution of grains in bi- and tri- modal powders

Here are some considerations regarding the grain size distribution.

This model indicates the theoretical limit for the addition of smaller powder. Exceeding it perturbs the optimal configuration. The addition of smaller powder is also undesirable for the reasons indicated below.

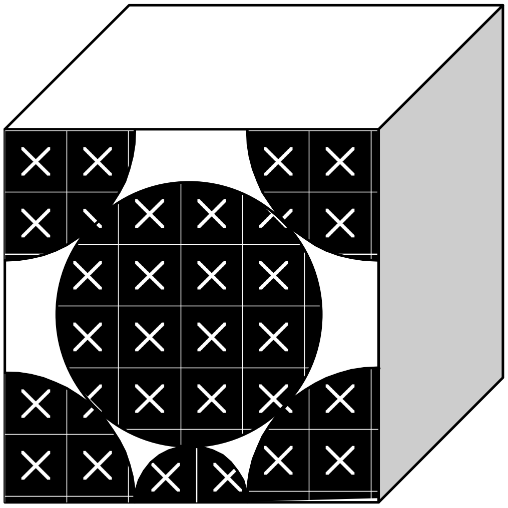


Figure 15 - The FCC packing of spheres

The main examined powder is spherical. The maximum theoretical packing of spheres is in the shape of a tetrahedron, a three-dimensional geometric figure with four faces of equilateral triangles. The four spheres, of the same radius R are supposed to be tangent to each other, each touching the other three, and the four vertices. Eight of them can be combined to make a cube. In Figure 15, one face of the cube is displayed with a section of five spheres, 4 quarters and 1 half. The equivalent volume of eight spheres of radius R can be contained in a cube.

Several spaces are left for spheres with a smaller radius.

Four more spheres can be added to each of the two faces and one in the centre of the cube of radius r_1 and eight more of radius r_2 can be added in the centre of each tetrahedron.

The theoretical density of adding four spheres of radius r1 and eight of radius r2 is respectively around 2 and 4% more.

The total theoretical achievable density mixing the three sizes powders is

$$\rho_t = \rho(R) + \rho(r_1) + \rho(r_2) = 75\%$$

The maximum practical density, achieved after tapping, is usually much lower, about 60%. This has been confirmed by all the tests, including those with the different powder mixtures printed.

Theoretical benefits of the addition of smaller powders

What do we learn from this? It is theoretically possible to increase the packing density with bi- and tri-modal powders, but only by a few percent. On the opposite, it is necessary that the small grains assume the required position, which is very unlikely to happen. The density cannot be increased a lot further by adding small size grains for two drawbacks:

1. because the probability that they go into the right place decreases (and it can be calculated theoretically), and if they go in the wrong place they disturb the whole configuration.
2. And also the more complicated the size distribution the more the work to make it.

An alternative is to add only a very small powder of the same size (e.g. 20 and 1) to fill almost all the empty space. But it is more difficult to spread (absorbs humidity and electrostatic effect, and it stick to the roll) and may give sintering problems.

Therefore, it is more probable that the addition of small powders will disturb the theoretical maximum packing configuration. This is practically shown by an increase of density. Another drawback of creating artificial compositions, beside the technical problems, is the difficulty in obtaining a uniform distribution and to avoid segregation.

Other effects of adding small powders

The benefic effect of the small powder addition is twofold:

- not only for the incrusting of small grains among the large ones on the line surface,
- but also from their cushion effect from the inside. The line is compressed by the liquid until the surface become smooth and inside the line grains are rearranged to support this phenomenon. The smaller ones have a higher mobility and more degrees of freedom because they can also fill in the small spaces among large grains. For this reason, they allow the large grains on the surface finding the optimal position (a smoother surface) by pushing them.

This effect is shown by more regular lines (not only better surface) obtained with more and smaller powder (25% of 2.5 μm with respect to the 10% of the -5 μm or to the 12.5% of the 5 μm).

The plan of experiments

Several tests have been carried out and repeated to explore the more suitable range.

The upper and lower bound have been determined with the following considerations

1. the max Ds is given by the maximum primitive ball, which correspond to ...
2. There is no theoretical lower limit for Ds, but productivity constraints.

The frequency is upper limited to 1.5 kHz.

A second group of test was carried out to assess the effect of the primitive ball time. These low speed/frequency tests have been carried out again to assess the effects of the Ds and of the frequency.

A first set of experiments has been conducted with the previous version of experimental facility: the 3DRing machine.

The first approach was a sort of mapping of the more suitable range of

1. the effect of the parameters
2. the effect of the material system
3. the effect of the distribution size

The parameters range has been quite wide.

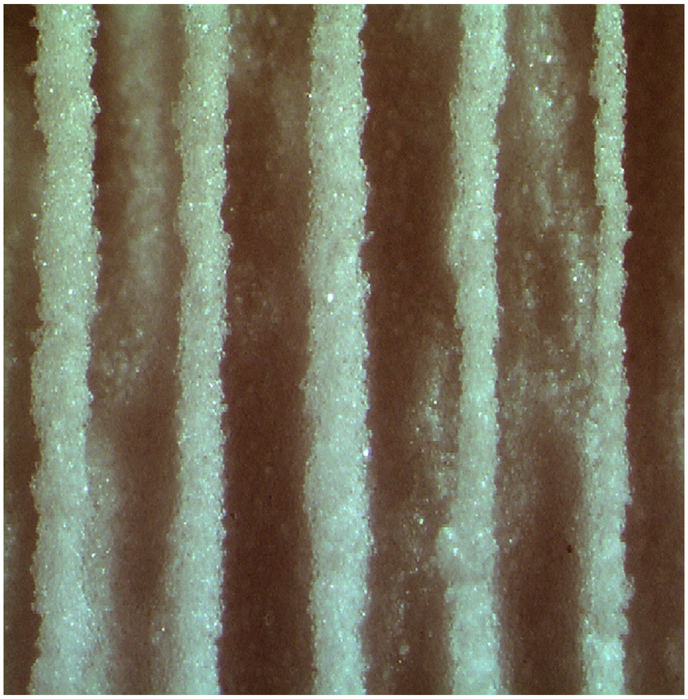


Figure 16 - A low speed test performed on 20 μm spherical alumina. The speed is 0.7 mm/s

Table VII - Experiments. The range of the main parameters tested

Drop spacing:	3 - 120 μm
Fast axis speed [mm/s]:	1 - 30 (3DRing) 0.1 - 0.2 (3DRing slow axis) 0.7 - 10 (3Dline)
Drop frequency:	5 Hz - 1.5 kHz (1.35 kHz continued)

Low speed tests

In Figure 16, the effect of the very low speed is shown. First, no line quality improvement is achieved, fortunately! Because productivity would be very low. Second, it looks even worst. The irregular surface of lines is probably due to more grains stuck on the surface, attracted by the liquid penetrated deeper into the bed for capillary. Some liquid penetration for capillary has been observed by [Straube00]. Of course, it happens in all directions, but at normal speed the amount of liquid penetrating in the direction of the line produces a positive effect, because new drops find already a liquid/powder mixture and this helps a better rearrangement.

Printed beds

The bed displayed in Figure 11 is an example of low cohesive powder that fall inside the grooves covering almost completely the lines.

Chapter VIII.

THE MULTI-PASS METHOD

Introduction

This new method has been discovered by chance, printing one line twice (as shown in the report) saved, for a switch failure. The line obtained was a little larger and smoother than those close to it, which were printed using similar parameters. Further tests have been then carried after the following two considerations:

- When spreading water on a sand bed (as it can be experienced by anybody on the beach) the liquid, penetrating in, smoothes the surface.
- In particular, drops (or a sequence of drops) in a powder bed tend to assume a round surface, e.g. a sphere (or a cylinder). By assuming this shape they rearrange the powder/liquid mixture, reorienting the grains. If one or more drops fall in the same place, the process is repeated and the primitive becomes more regular.

In the case two lines are very close they merge. When trying to make a line out of the scarce powder between two separate lines, it has been observed that because of the excess of additional binder printed that the three lines assume the shape of a single thicker line.

This demonstrates the strong tendency of assuming a circular shape, in order to minimise the surface energy, by rearranging the binder-powder mixture. Of course the line resulting from two touching lines displayed in figure is irregular, but its surface is smooth and almost thoroidal. The layer formation is however a topic for future work.

Definitions

This so-called multi-pass effect was exploited in different ways, as multi-nozzle, as multi-line and multi-pass-layer.

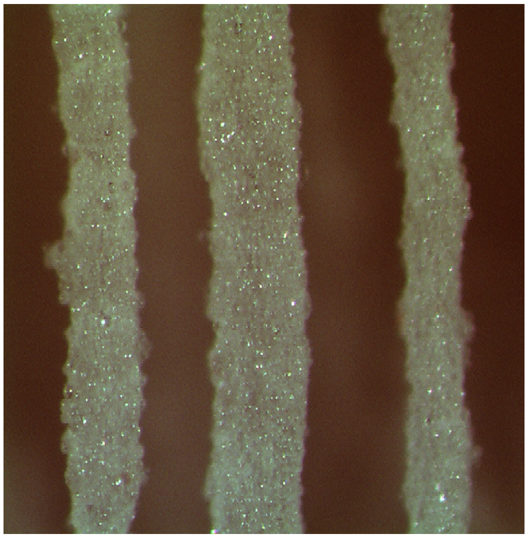


Figure 17 - Benefit of the multi-pass (center line):a line printed in double-pass between two standard lines

Multi-nozzle: by having two or more printing nozzles aligned. Of course, this is only possible in raster printing, because only in this configuration nozzles are on the same trajectory at all times. This was easily implemented with the printhead used by connecting two nozzles to the same wave generator.

Multi-line: by printing a line and passing over again after it has been printed, for instance with a return trajectory that passes over the same line twice, or going back and forth more times. Another way multi-line has been tested is making rings by multiple revolutions.

Multi-pass layer: an additional pass can also wet a layer after completion in two ways, in phase, passing over the same lines, or passing over their intersections or in any different combination one can imagine. This potentially very powerful technique is proposed here as is and it has not been tested in this project due to a lack of time.

Beside the different hardware implementation of the multi-nozzle and the multi-line methods, the effects are very similar because the time difference is not relevant, so in the remainder they will be generally addressed as multi-pass.

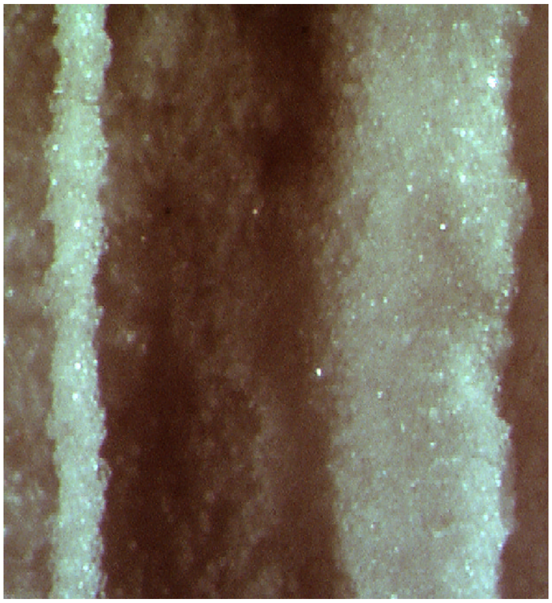


Figure 18 - The largest (multi-pass) and the thinnest lines in the same bed

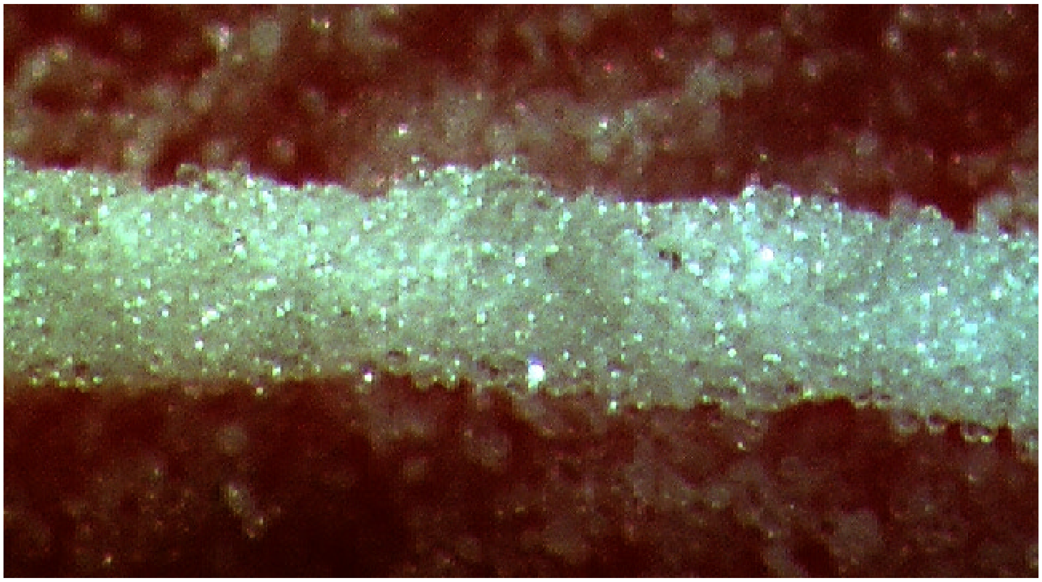
The multi-pass phenomenon is also a confirmation of the importance of the powder mobility. The addition of more binder to an already formed line gives space for the powder reorganization, while the liquid tends to assume a regular shape.

The nominal drop spacing is maintained in the multi-lines by using an actual value

$$Ds^{*} = Ds \times N_{passes}$$

in order to have the same binder input. However, the minimum amount of binder necessary to trigger the "good line" formation should be provided, so the maximum Ds for single lines cannot be exceeded.

A line as thin as 130 μm has been obtained in double pass with a 25 Ds.



Again, there is no lower limit for the drop spacing. The only problem is the increase of the line width. No specific tests have been done, but a line 400 μm thick was obtained in two passes. An application of this method could be printing cylindrical cores of a given diameter.

Experiments with the multi-pass technique

Some defects are typical or occur more frequently with this technique, which is characterized by the addition of more binder. They are described in the Chapter on the Classification of defects.

The following effects have been also observed.

A particular case of multi-pass: the flattening effect

Multi-line on a mixture of -10 and 20 μm spherical alumina powder in a 2:1 weight ratio had the effect of flattening the line. Additional passes enhanced this phenomenon. In addition to that, the line aspect got worst as a side effect, and became more irregular, which was not the desired result.

Multi-nozzle on the same mixture did not yield an improved shape, and lines were slightly more irregular.

The printing parameters were:

Fast axis speed, S_f [μm/s]	400
Drop spacing, D_s [μm]	10

Theoretical considerations

The longer printing time in the low speed tests, make the line dry before the sequent pass.

The two effects observed on the mentioned powder mixture are probably due to a prevalence of small grains, which make the line structure more deformable under the hydraulic pressure.

This hypothesis is confirmed by the same type of test performed on a 20 μm powder whose lines remained round, larger and smoother. The fast axis speed was also very low and the test has not been repeated at high speed so it is not known if the effect is also a consequence of the low speed.

The flattening effect is particularly useful to achieve better surface finish when printing the last layer. It can be used to reduce the inter-lines roughness according to special patterns, eventually doing the multi-pass (also) between the already printed lines. This represents an interesting topic for future investigations.

Chapter IX.

CLASSIFICATION OF DEFECTS

Direct observations

This is an important part of the proposed methodology. All observations should be documented and recorded for future references.

Introduction and definitions

A very powerful tool has been developed to help the designer optimizing the printing parameters. The problem arose in the definition of a "good" or of a "better" line. Sometimes a line is better under some aspects and worst under other. However the main purpose of the classification is not only defining more objective criteria, but mainly trying to find a correlation between

defect type - cause - remedy

Of course, this approach can be extended to any material system adding, removing or changing some of the defect classes.

The main entries of the classification are: characterization, observations, possible causes and remedies.

Many of defects are due to bad powder spreading and can be often avoided with a careful workshop practice. But it is important to identify them for the novice or to check of any routine errors.

In present study, the importance of improper sieving has been identified just with this method so apparently worst lines have come out to be better after filtering the observation by identifying the cause of the bad aspect. In particular, adding a smaller powder usually produces agglomerates due to the presence of humidity or insufficient mixing.

The characterization of defects is very important for their identification and to find a correlation with the printing conditions. In present study, the importance of improper sieving has been identified just with this method so apparently worst lines have come out to be better after filtering the observation by identifying the cause of the bad aspect.

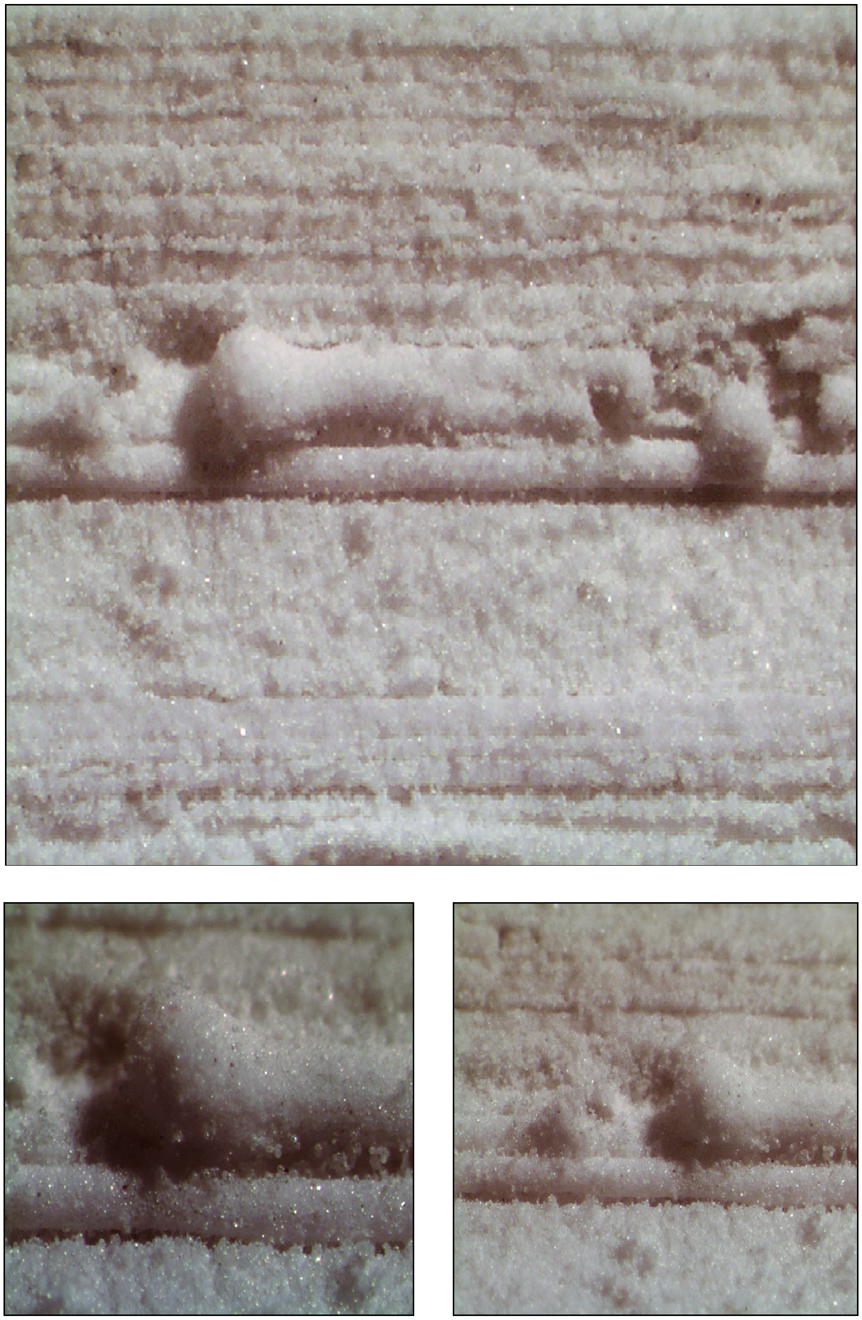


Figure 19 - End ball, detail of the ball and of the line interruption

In particular, adding a smaller powder usually produces agglomerates due to the presence of humidity or insufficient mixing. And also, for the absence of objective criteria, at some point during this project it was even not possible to assess which line was better between those extracted from two different beds printed in different in different conditions, in order to improve the process performance with the given material system.

Description of the morphology of line defects

End ball

End ball example and detail of the ball and of the line interruption (Figure 19). Good line and ball can coexist. It is considered an exception for the rare occurrences and has not yet been investigated.

The ends of lines (Figure 19) have a semi-spherical shape too. The first end in particular has a sometimes a lower depth than the rest of the line, and this shows that the penetration of lines is usually higher than single (first) drops.

According to [Straube00] when printing lines, new drops impact the powder-grains mixture and the ejection phenomenon becomes less relevant. This is confirmed by the better line quality in the experiments at very low drop spacing, e.g. 3-5 μm, where the overlap between successive drops is 90%. The drop impact can be seen instead as a drop of liquid feeding a cylinder of liquid and powder.

For new drops, finding a line already formed also helps assuming a regular shape.

With these low parameters, low drop spacing and frequency, capillary becomes important too because the liquid has more time to penetrate in the loose powder. Considering the productivity requirements and that low frequency does not improve the line quality, it does not have a practical interest.

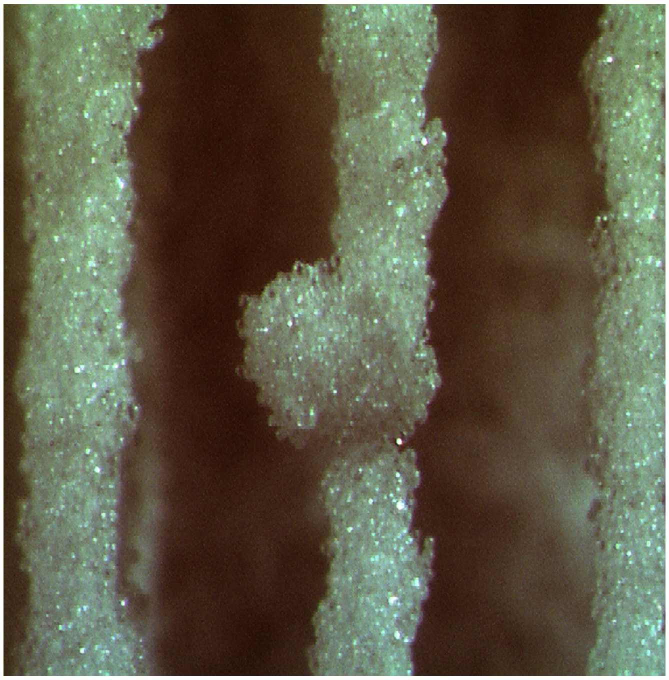


Figure 20 - Evidence of a clump incorporated in a thin 20 μm spherical alumina line

Irregular axis

The irregular axis is due to finding the easiest path for the line. It does not follow the printed drops because it may be easier to flow in an area where there are less or more voids according to the prevalence of the capillary effect, so it is probably more relevant

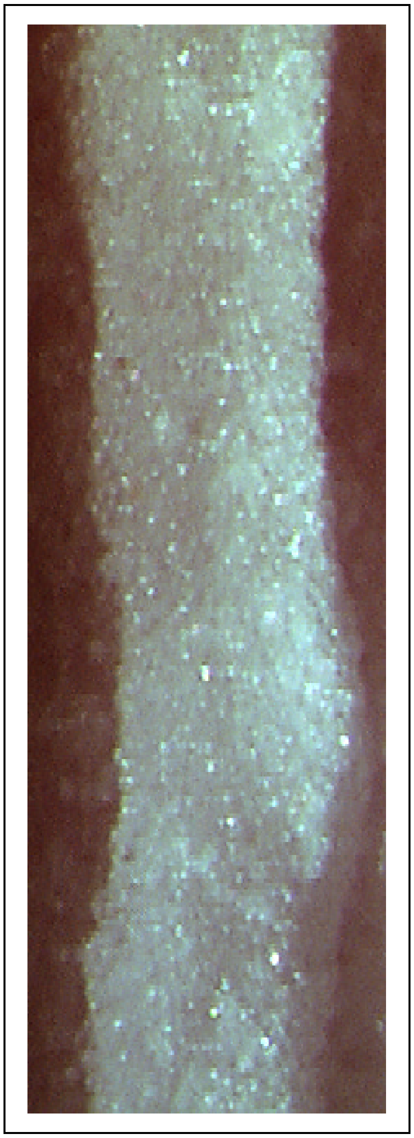


Figure 21 - Line with irregular axis

at lower speed.

Irregular line surface

On a macro scale it is due to insufficient binder input, e.g. for excessive drop spacing.

The presence of many grains out of the average cylindrical envelop line denotes that they are stuck to it for some reason and did not take part in the liquid-mixture rearrangement. The main reason is the low powder mobility.

The same effect has also been noticed in the experiments at very low speed. An example and an explanation of this phenomenon can be found in Figure 16 on page 60.

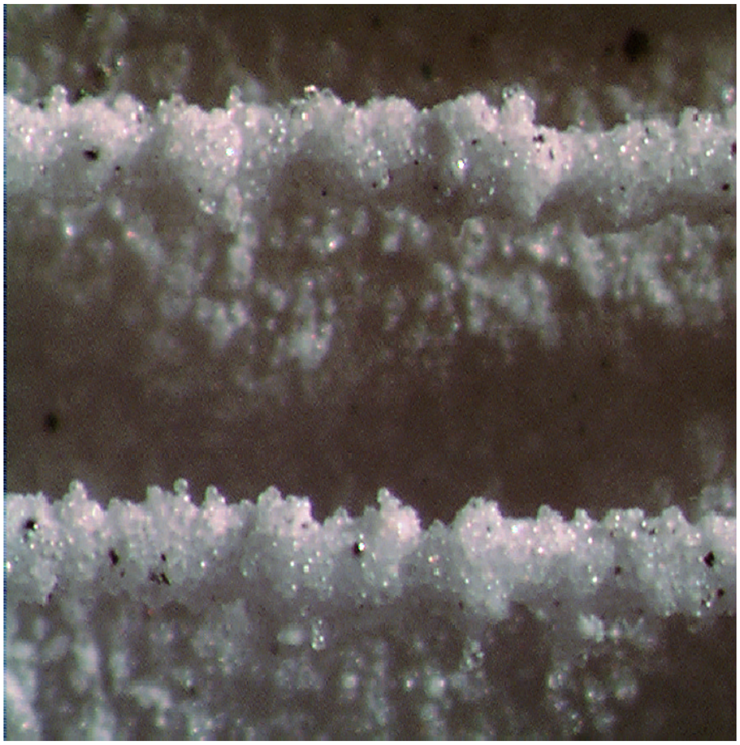


Figure 22 - Lines printed with a drop spacing of 35 μm

Clumps

They are one of the most common macroscopic defects. The trained eye is able to see them almost in all lines. Seeing them has been a key to understand the effect of mobility. A large clump in a thin line is shown in Figure 20. It is interesting to observe the effects of the small clump in Figure 23. It has about the same size of the line, so t produces a distortion of the line axis, deviating the path of the liquid.

Raised lines (spaghetti)

This defect sometimes occurs on the first layer on the Alpha Machine. It is called "spaghetti" in jargon. Lines make a bridge coming out of the bed. Its origin has not been found yet. The remedy consists in making the layer adhere to a background.

In this study, it occurred on some lines of a couple of beds only. It has been observed with thin and thick lines, at high and low drop spacing, at low and high speed and at low and high frequency. It is due to an increase of the length of a line and it has been noticed during drying. It would have been challenging trying to understand its origin, but it was so rare that no sufficient elements could be collected.

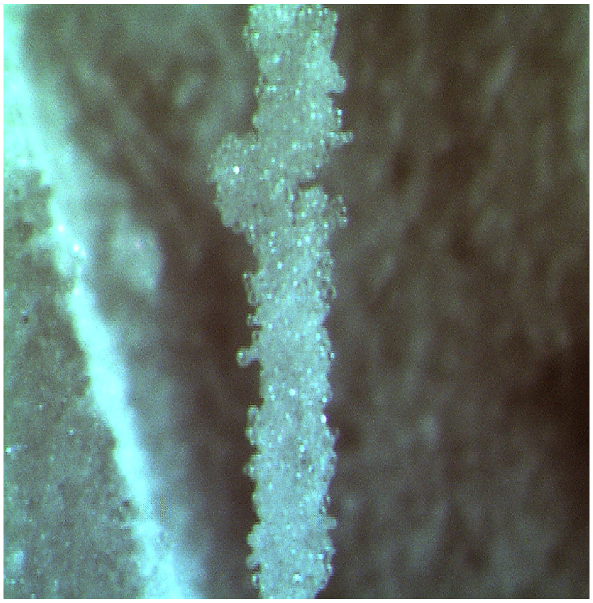
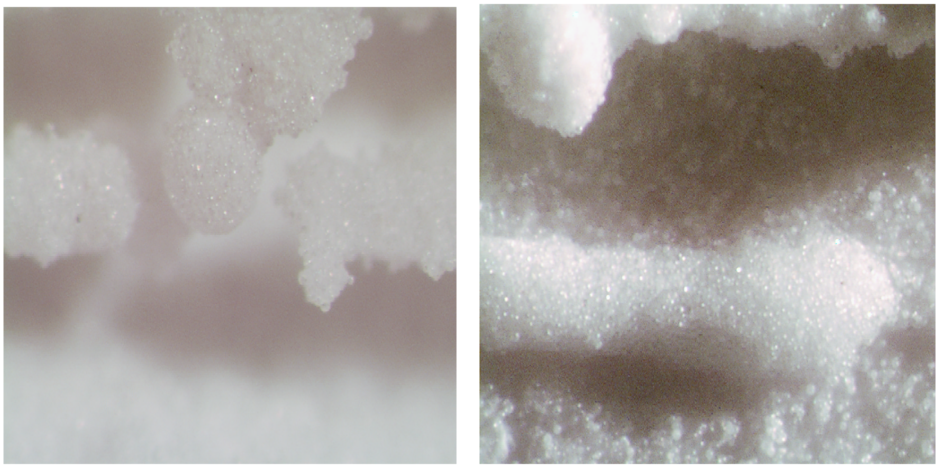


Figure 23 - A small clump incorporated in a line

Typical line defects with the multi-pass technique

The "size undulation" defect in the multi-pass method

One drawback of the multi-pass method is the presence or the enhancement of the defect "size undulation", a symmetrical repeated line size variation. It is probably due to



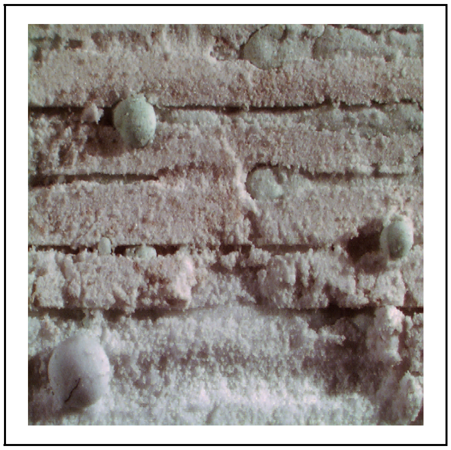
an amplification of the axial displacement of grains helped by the presence of the liquid addition before it dries.

It is also possible that this phenomenon is the enhancement of differences in the powder bed density, when it is symmetrical. When it is asymmetrical, it is more due to the presence of clumps.

The balling effect

There is a direct observation related to these theoretical considerations. The presence of small and large bubbles can be considered as a case limit of very amplified undulation. The fact that they share the same nature and that they are due to similar causes is confirmed by their coexistence in all the observed beds. Bubbles can be of different types:

1. very large, symmetrical increase or reduction of the line size, starting from half the



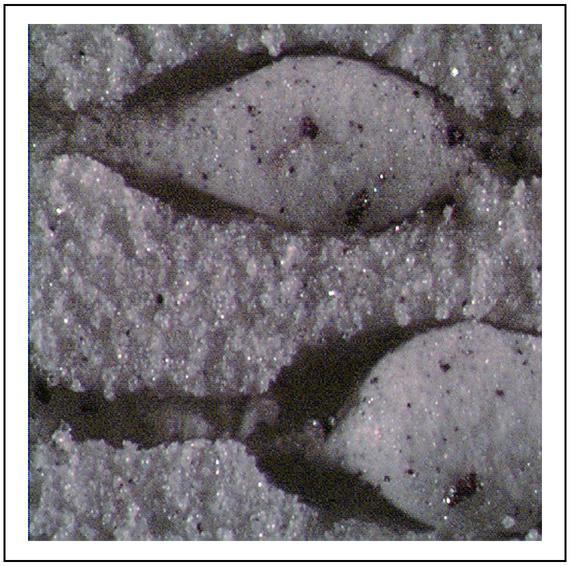
line size or

2. line interruption with a spheroid end or
3. a separated bubble.

In both cases the axial displacement of grains has been clearly observed through the shape of grooves containing lines.

The ball-state also has lower energy and is more stable than lines. It probably depends on the low wettability of the powder as it is on or off for different powders with the same parameters. It has been observed that it does not depend on the drop spacing, so it is not related to the amount of binder.

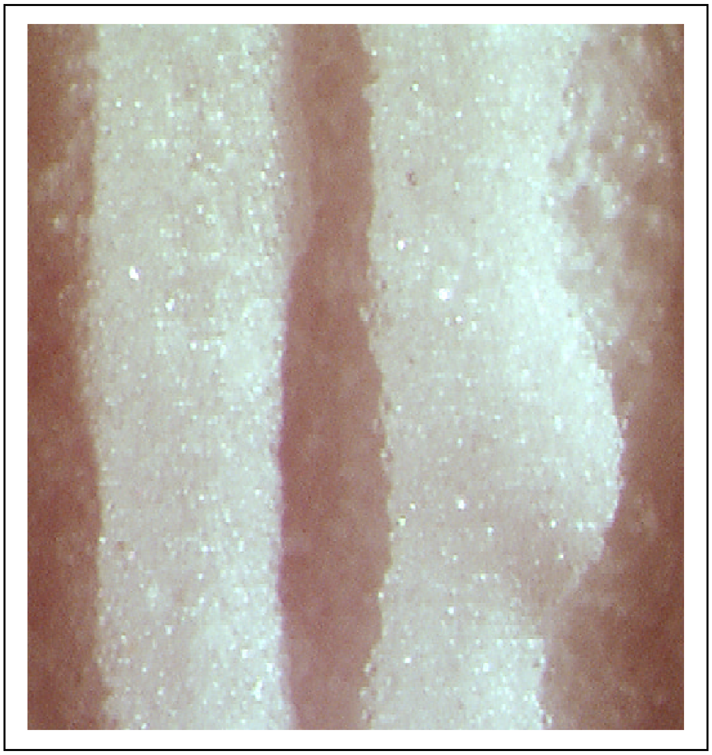
The presence of balls instead of lines is called balling. It is also common in CJ printing where it occurs for a similar causes [Fan95]: the non-wetting of the powder caused by the very high drop frequency.



Other possible defects

Large smooth balls (figure) come from clumps that are smoothed by successive passes.

Irregular axis can be due to enhancement of the previous defect or to incorrect realignment in successive passes.



The peeling off of small particles

It has been observed at the optical microscope that the top of lines after multi-pass may be less even than the rest. This observation has been confirmed at the ESEM as the absence of small grains that are probably peeled off by the liquid addition.

Important differences between similar line defects

Bumps, small protrusions and external clumps

For the case of few grains, small protrusions and external clumps coincide. For more grains the difference depends on the shape of the cluster, long and narrow for the first and more round for the second. The reasons why grains tend to stick in these two different ways are not clear, but the remedy is the same.

The main difference between bumps or small protrusions and external clumps is that the formers are integrated in the line and take part in the line formation rearranging, while the latters are stuck to it and are only partially invested by the binder. Evidence of this is given by the redistribution of small particles in the case of bumps only.

It would be difficult to measure the force of contact to assess how much an external clump is stuck. Direct observation demonstrates that they are really stuck by the presence of binder between it and the line. Of course, both defects are detrimental for the surface finish. And also if the external clumps could be theoretically easily removed from the final surface, during the addition of other lines they would interfere anyway with the regular layer formation.

Bumps and bubbles

The more evident morphological difference between bumps and bubbles is the higher surface roundness of the latters. This is due to a different action of the binder on the powder, which is more limited on clumps at the origin of bumps. The formation of bubbles is also bound for some reason to the particular powder configuration, like a local density variation, which affects the movement of the liquid mixture for capillary interaction or for other unknown effects,. But in this case the powder is free to move and is rearranged by the liquid in order to achieve a lower energy level in a different configuration than a cylindrical line. In this case, a still wet bubble, touched by a line being printed next to it, has been incorporated in order to reduce the whole surface to volume ratio.

Bubbles, line interruptions, balling and size undulation

It has been observed by [Straube00] that the drop impacts in a liquid-powder mixture, because the liquid penetrates for capillary and advances. However, in the presence of a bed discontinuity, penetration is stopped and consequently an interruption may be produced. For the tendency of the liquid to rearrange in order to assume a round surface, an axial movement is produced, eventually accompanied by additional fluctuations, which determine the presence and size of the end bubble. The effect of the axial movement was also shown by the presence of some dirt in the line. The liquid mixture flow has been temporarily stopped by that element and the line width has increased for the consequent increase of the volume of liquid due to the stagnation.

End bubbles can be observed also at the beginning and at the end of a line both when the printhead is stopped and when the bed boundary is exceeded.

The presence of one or more separate bubbles is very common in the CJ process where the high drop frequency does not allow the binder-powder mixture to advance quickly enough.

The importance of the axial movement of the liquid and of the continuity of feeding was shown by printing a "grid" where the lines printed rotating the bed by 90° after the first lines have a very poor quality and are worst than the perpendicular one printed with the same parameters.

Methods for remedying line defects

The main process parameters

In order to find the best line and to understand the process phenomena, specific tests have been carried to assess the effects of each parameter. A short list of parameters is available in the following Regarding the power bed, it should be noticed that compression has two effects:

1. increasing the powder density and
2. the regularity of the distribution.

Only the second effect is desirable and can be achieved through vibrations instead of compressing the bed with the roll used for spreading. In this project, with the manual spreading technique, vibrations have been produced by tapping the bed support.

Table VIII. A description of the more relevant and non-obvious effects is available in the chapter "Finding the perfect line"; an interpretation is available in the chapter on the "Theoretical model".

The following list is also a memorandum of available degrees of freedom when testing a new material system.

In many cases the expected effect (purpose) was unknown or different *a priori*.

Regarding the power bed, it should be noticed that compression has two effects:

3. increasing the powder density and
4. the regularity of the distribution.

Only the second effect is desirable and can be achieved through vibrations instead of compressing the bed with the roll used for spreading. In this project, with the manual spreading technique, vibrations have been produced by tapping the bed support.

Table VIII - Outline of the main process parameters tested and resulting effects

Action	*Purpose*	*Actual benefit*
Changing fast axis speed and drop frequency	changing line size improving line quality	changing line size improving line quality
Mixing different size powders	obtain smoother line	obtain better powder bed
Sieving	eliminate miscellaneous unwanted elements	eliminate clumps
Coating	changing the wetting ability	reduce the inter-grain friction
Heating the powder to reduce humidity	non sticking powder, easier spreading	non sticking powder, easier spreading + avoid clumps
Tapping the powder bed	increase the powder density	obtain more regular powder distribution
Heating the powder bed	keep the moisture out	reduce the friction
Re-printing the same line	unknown	improve surface finish

Table IX - Classification of defects on 3DPrinted lines

	Defect	**Morphology**	**Possible cause**	**Remedy**
①	Irregular width	> 1/3 line width	Imperfect spreading/packing	Tap/Heat the bed Coat the powder
②	Bump	< 1/3 line width	Clumping of large grains before spreading	Sieve the powder
③	Small protrusion	1 - 10 grains		
④	Bump	< 1/2 line width	Clumping of small grains	Improve mixing
⑤	Irregular surface	Regular width	Missing grains	Add smaller size powder
⑥	Irregular shape	Straight axis	Lack of binder	Reduce drop spacing
⑦	Large bubble	Smooth surface > 1/3 line width	Excess of binder	Reduce drop size Increase drop spacing

The classification of line defects

Most information described in this chapter is summarized in Table IX with some examples images in Figure 24.

The relative size of defects is qualitative, to give an idea of what they looks like and to have a scale when comparing similar defects.

This expandable classification can be used as a tool for the process optimization and applied in the form of a decision tree.

This tool can be extended to other material systems.

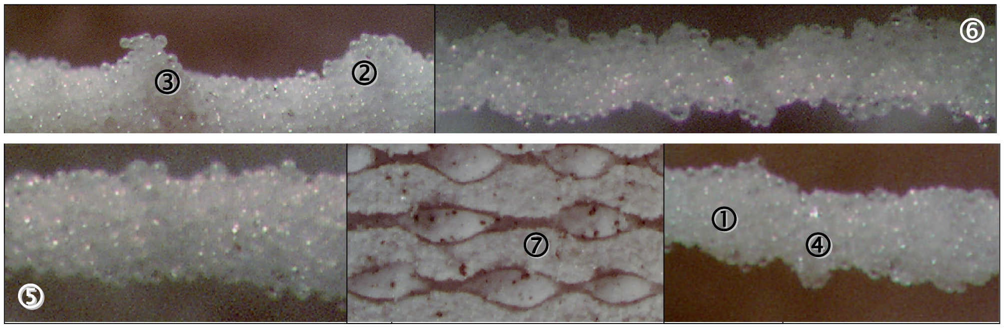


Figure 24 - Examples of defects in the classification

Chapter X.

FINDING THE PERFECT LINE

Experimental observations and discussion

The effect of drop spacing

It can be noticed that at higher drop spacing, lines are thinner so they have a higher surface to volume ratio, so the surface forces that act to rearrange the powder are more relevant. However, on good quality lines, an upper limit has been found for the drop spacing. The insufficient binder input does not allow the basic mechanism for the line formation to occur. The magic number is 25 μm and 20 would be a safe limit. This value probably depends on the drop size and on the material system. No lower limit has been found going down to 3 μm.

Lower drop spacing lines use to be perceived smoother for optical reasons, because of the larger line width and lower percentage error. Their quality is also better, probably for two reasons:

- an averaging effect of voids distribution;
- the powder re-organization is more effective with more material.

The negative effects of the low drop spacing are the lower productivity and the larger line width that affects the roughness of the final part. Therefore, when the line quality is not crucial, to increase productivity a compromise could be found investigating the 25 μm and up area.

The line width as a function of the drop spacing is displayed in. The effect of the voltage on the drop speed and size is not known in all the range displayed. There are probably resonating effects (at 15.5 V) producing a non monotonous behavior that is reflected on the line width. However, at constant voltage a quadratic dependence as predictable by geometric considerations is shown by the line of tendency in all cases.

Effects of the addition of smaller powder

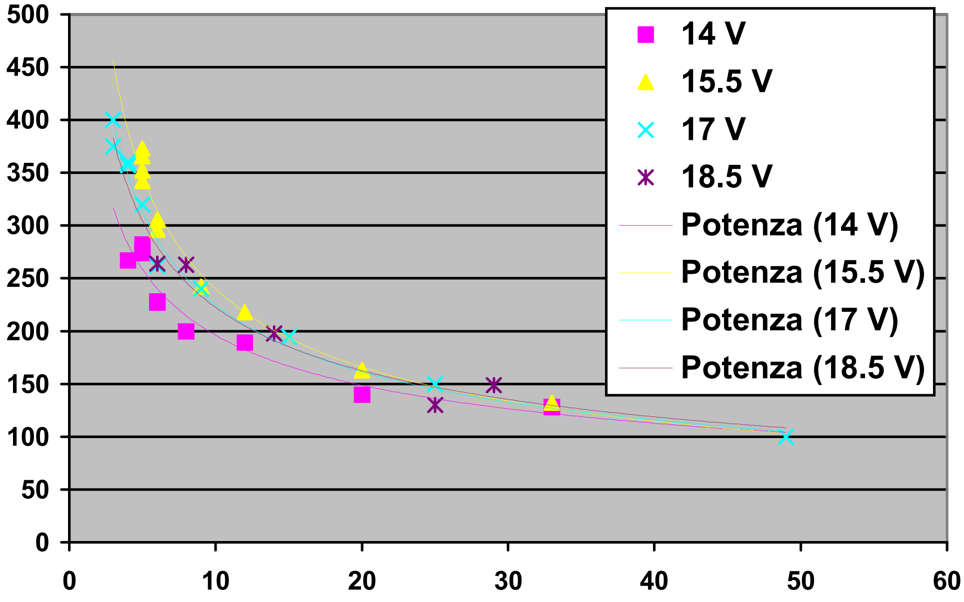


Figure 25 - The effect of Drop spacing on the Line width for different nozzle Voltages

One of the key actions to improve the line quality is finding the optimal mixture. The main purpose is to fill the empty spaces among large grains as explained in "A more accurate estimation of the on theoretical R_a on perfect lines (cylinders) made of spheres is also possible with easiy geometrical considerations.

The theoretical spatial distribution of grains (page 57)". This is not always possible.

A consequence of the higher density of line is the higher strength. It has been verified in a test, with the addition of 30% of a -5 μm powder, by the high resistance opposed to the air flow during the powder removal. Those lines where still irregular for the drawbacks of the addition of small powder indicated in the following Table X.

Table X - Drawbacks of adding smaller powder

It has a greater tendency to absorb humidity and make clumps.
It is more difficult to spread[5] because it tends to stick for the presence of humidity or electrostatic forces.
It may cause sintering during firing producing shrinkage and deformation of the final part.

Very small grains have a positive effect on the surface finish of a line locally, in the sense that if defects are present, they smooth it. Defects may come from one of the above-indicated phenomena.

This picture shows a large fragment of bed that represents the negative of the line near to it. The compactness of the bed without any additives is due to the moisture absorption by the small powder. The consequent low mobility makes line irregular. The locally smooth surface can be observed though.

In this picture, a lateral view of the same line shows the different smoothness on the top and on the bottom due to the different powder mobility.

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[5] For this reason the slurry-based 3DP technology has been developed.

It seems that the addition of smaller powder can have two opposite and both positive effects:

- on the dry powder it can reduce the apparent density when going among large grains;
- they use to increase the tap density by filling the empty spaces among grains and also the density of lines by filling the empty spaces after compression, since they have a higher mobility in the powder-liquid mixture.

In the case where the density of the original powder is reduced by the addition of the smaller powder, it seems that the small grains are not filling the empty spaces but instead they are pushing larger grains apart. In this configuration, they can be seen as ball bearings and they increase the large powder mobility transforming the drag friction in revolving friction. In this sense, the optimal size of the smaller powder is such that it does not have the indicated drawbacks and it may produce the above-indicated benefits.

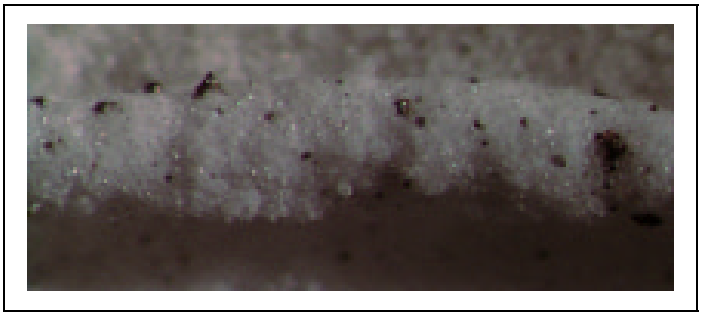

Figure 26 - A side view of a line. The top is smooth and the bottom is not

A measure of the "ball-bearing effect" of the small grains should be observed in terms of grain mobility, by a diminution of the angle of repose, in the case where the density decreases.

Table: comparing the density and the angle of repose for good lines.

The above considerations are helpful for understanding the different effects of the addition of the same weight percentage of say a 5 or a <5 powder. The different size distribution may affect the powder properties according to the behavior of smaller grains.

A concentration of small particles has been observed on the line surface, making it smooth by filling most voids. It is still not clear where to they come from, inside the line or from outside it, from the bed near it. There is one hypothesis. For the lower tendency of small grains to be engulfed in the liquid, they reach the line after the large ones. When the liquid dries or moves to the next drop and the line is compressed, the smaller grains are deposited on the line surface.

The most important effect of the addition of small powder is however on the large grains movement, because also lines with the small grains smoothing their surface still have a low quality if the configuration of the large grains is irregular.

Evidence of the importance of the grains mobility

The measurement of the powder mobility is a dynamic one, and so the angle of repose is, because grains are moving with respect to one another.

It has been observed that lower density and angle of repose yields higher mobility.

It has been found that if the powder grains have a higher mobility, better lines are printed. There are several ways to increase the powder mobility and to assess it.

The engulfing force can be very slightly increased by coating, so it can be assumed as constant. Consequently to affect the process the grain mobility should be increased. From these considerations **the theory of grains mobility** follows.

The friction depends on the following factors and can be reduced as summarised in Table XI.

Table XI - Increasing the grains mobility

Factors influencing the grains mobility	Observations
inherent alumina friction	can be reduced with coating or by heating
grain shape	minimal for spherical powders
low bed density	the powder should not be compressed powders with a lower inherent apparent density are preferable

Regarding the power bed, it should be noticed that compression has two effects:

1. increasing the powder density and
2. the regularity of the distribution.

In this case only the second is desirable and can be achieved through vibrations instead of compressing the bed with the roll. In this project, with the manual spreading technique, vibrations have been produced by tapping the bed support.

Methods to increase the powder mobility

A proof of the importance of the powder mobility is the presence of clumps, which are a limit case: the absence of freedom, being grains stuck to each other.

Different 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.

Measuring the angle of repose, which is a specific test to measure the powder flowability, shows the positive effect of both methods. However, it seems that flowability is only a sufficient condition, and not a necessary one, since good line have also been obtained with powders characterized by a bad angle of repose.

On the opposite, a direct observation of the powder bed is not able to provide information on the powder mobility.

Coating the powder

The main intended purpose of coating the used powders is to reduce the surface friction through the addition of a polymer, which use to have a lower friction coefficient. Achieving this effect is not obvious, because the friction reduction depends on the grain roughness before and after coating. Better results have been obtained with very low thickness coating (few molecules), e.g. with a low concentration in the water solution of the additive. The tested additives are commercial surfactants (Duramax 3007 and Darvan C). Their chief intended use is to have a suspension of particles, by charging their surface and having them repel to each other. This action is only possible on small size (weight) particles, < 2 μm, so there is probably no other effect than the friction coefficient reduction on the large ones.

Only the large (20 μm) grains have been coated, for the following reasons:

- coating takes time for the preparation, one night to dry, and additional time to crack and sieve the compact mass obtained, to get the single grains again. Many size combinations have been tried, so coating individually every mixture would have been excessively time consuming;
- coating all the numerous additives, in addition to be time consuming is also a difficult task, again for the separation and sieving of small stuck grains, after drying;
- some effects on the movement of small grains are also obtained, because the surface of the large grains is also charged when it gets wet by the binder.

The coating will act both on the wet powder during rearrangement inside the line (for the friction reduction and the repulsion effects) and on the dry powder between a grain being engulfed and the surrounding ones.

Duramax 3007

I used a 10% of 1 cl of alcohol (for faster evaporation) of Duramax for 0.5 g of 20 μm powder. I removed the excess of liquid before drying. Considering the low powder surface and that I need only one layer of polymer 1% should be enough. And also it does not evaporate so it all remained on the grains. The powder was then dried at 80° C in oven and sieved with a 325 (44 μm) sieve.

With an excess of Duramax 3007, the coating get the flowability of the powder worst. The powder also tends to stick. Sticking is also greatly increased when heating the bed to increase the flowability, probably for the polymerization of the Duramax.

The bed has a typical pattern of groups of 5-6 grains bound together on irregular lines (Figure 27).

The loose powder is very hard to remove from lines with the usual air jet. I use a brush and the syringe end.

Lines are straight, but with that defect of "small protrusions" (due to the difficulty to remove single grains from the bed and include to the line).

The line size is also regular because of the low apparent and tapping density due to the same sticking problem.

Darvan C

From a previous successful experience [Baker97] a commercial surfactant has been used. A similar behavior as heating has been noticed. The coating is not visible at the ESEM because it is only a few molecules thick.

Three different concentrations of the surfactant have been tested: 10, 1 and 0.1 percentage vol. The first one is too high and produced a strong sticking problem on grains. The lowest concentration is sufficient for the intended purposes.

<u>Increasing the temperature of the powder bed</u>

The beneficial effects of heating to reduce friction of materials and to eliminate the moisture, which is naturally absorbed by the small particles from the environment, are well known. It is not clear if the higher mobility is mainly achieved for the reduction of

Figure 27 - Bed of 20 μm Alumina powder coated with a 10% solution of Duramax 3007. Clusters of 5-6 grains denote a sticky bed

the friction coefficient or for the reduction of humidity, but it has been observed that heating produces a beneficial effect.

The powder bed temperature has been increased in two ways, with an external lamp and heating the bed support. The first method has the disadvantage that the binder properties are also affected by the heating due to the small distance from the bed. A specific test was performed printing on the same bed at different temperature. Beneficial effects have been noticed at the optical microscope at higher temperature, though this is not evident from the acquired images.

Details of the two heating techniques

A 250 W halogen lamp has been directed to the bed during printing. Unfortunately, due to the lower distance between the powder bed and the printhead, this latter was also heated and the binder contained therein has spilled out probably for the reduced viscosity and for the increased nozzle diameter.

The final solution has been heating in an oven the bed support, which has been modified replacing the plastic parts with metal. The actual temperature of the bed and of the support (which are the same, for the small thickness of the bed, laying on the metal support), during and after printing, has been assessed with a thermocouple.

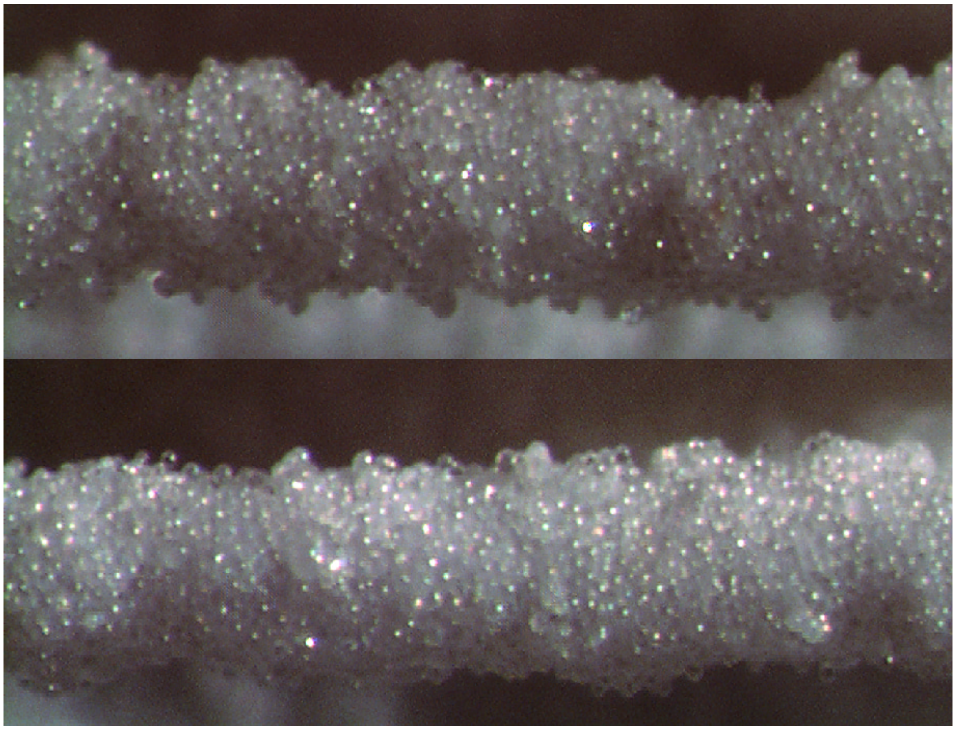

Figure 28 - Two lines from the same bed printed using the same parameters and at different temperature: room temperature (top), 80° C (bottom)

A specific test has been performed. The same bed has been printed at room temperature and then heated at 180° C and after cooling at 50° C. Slight benefits have been noticed that would not be evident in the pictures without the characterization of defects. In both cases the quality of lines is low, but at higher temperature (below) the greater freedom to rearrange of grains produced a more regular line width.

The importance of the powder ejection during the drop impact

The powder mobility is also important for the ejection of powder that helps the formed line being separated from the loose powder.

In this sense, the drop speed is important because it enhances the ejection phenomenon.

The powder ejection was observed by [Fan95] in the impact of one drop with the bed.

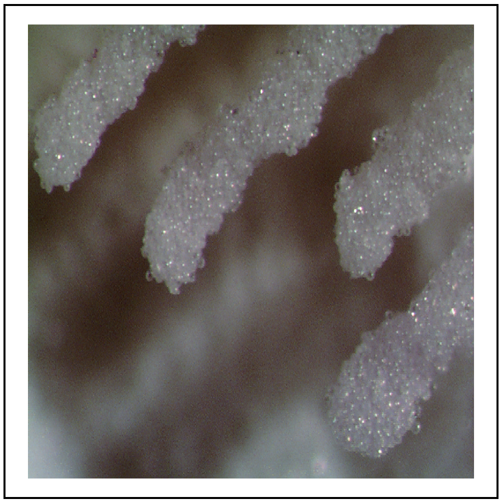

Figure 29 - End of lines showing an enlargement

It was also observed that single drops have a spheroid shape. The drop shape and the ejection effect have also been observed at the SEM.

For the presence of grooves in addition to a crater between the primitive balls, an axial movement is also supposed. The effects of this axial movement of grains inside the liquid are also discussed later.

Firing

Heating parts in a furnace at more than 1000° C is a fundamental step when manufacturing moulds, in order to allow the sintering reaction of the silica printed with the binder and to achieve a sufficient mechanical resistance. The effects on lines of firing have been investigated because it may cause the sintering of the smaller alumina grains and consequent undesired effects on the final part, like shrinkage or deformation.

It has been found [Bredt95] that firing as low as 750° C may produce sintering, as confirmed by the greater difficulty to remove the loose powder when blowing a low pressure air jet. More tests have been performed on both high and low quality lines at 800, 900, 1000 and 1100° C. In particular, no big differences have been found on the two parts of the same bed of good lines after firing at 800 and 1000° C respectively. In general, only good quality lines did not present the sintering problem between the loose powder and the lines. This was due to the gap between lines and loose powder as envisaged by the proposed theory. On the opposite, it has been confirmed that the loose grains tend to sinter to each other in all the observed beds (good and not) and also to the low quality lines.

Figure 30 - Bed fragments show the strong forces among grains. The lines are poor. With 20% 5 μm tapping

A possible definition of good quality lines comes from this behavior: good quality lines allow a complete removal of loose powder also after sintering. Under this viewpoint, the quality of lines becomes an on-off parameter, for the neat separation from the powder bed after its formation.

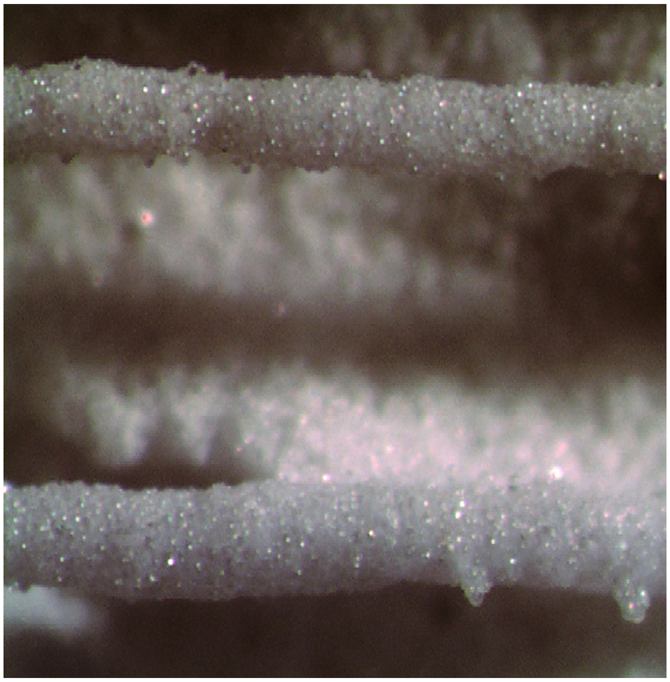

Figure 31 Sufficient and poor drop spacing

Chapter XI.

APPLICATIONS OF THE PROPOSED METHOD

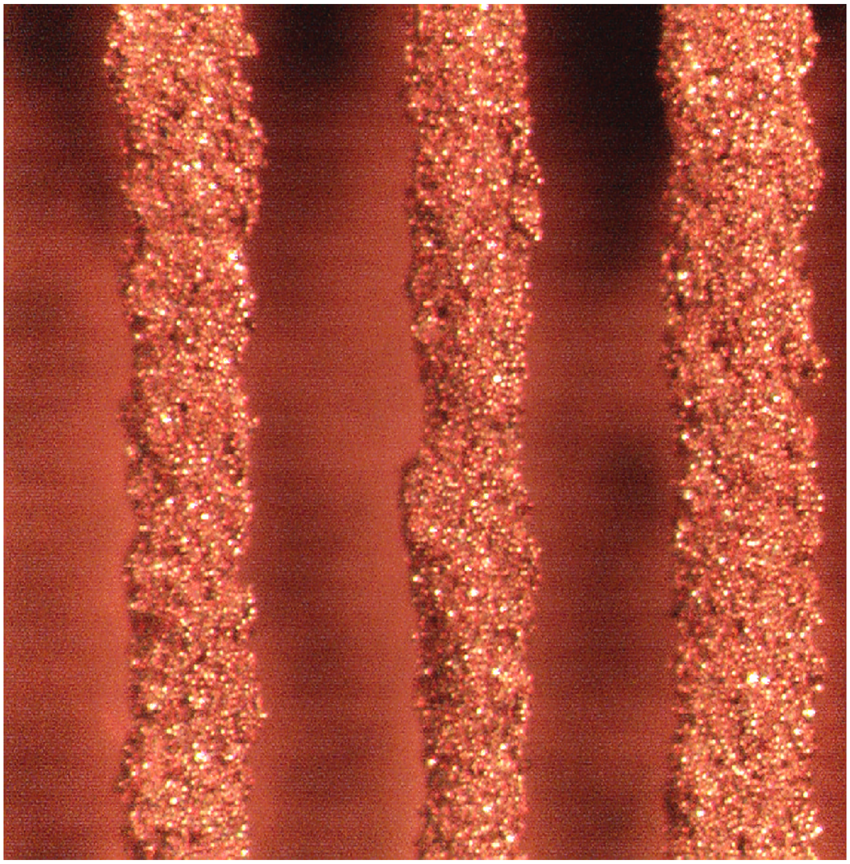

Figure 32 - Stainless steel 17-4 printed with the standard binder with no special care. Line width: 100 µm

Case 1: direct metal fabrication, 3DP of metals powders

Only five beds have been printed using metal powders. All are stainless steel. One was the 17-4 displayed in Figure 32. Four were 316L.

It seems that metal powder give better quality lines than alumina.

The main reason for that is probably the higher density, about twice higher, which makes the line penetrate in the bed absorbing more powder from the line bottom. Another possible reason is the reduced mobility, still bound to the higher wait that produces the following effect: only those grains that are subject to a high force from the liquid take part in the line formation. That high force is able to produce a better rearrangement, then the powder assumes the round shape of the liquid.

The 17-4 stainless steel

A test was performed on a new metal powder: a 17-4 stainless steel. displays how they printed without any special care.

The 316L stainless steel

Printed both with PAA in a 10% vol. water solution and the "standard" CSEG binder.

First worst line

Figure 33 - The tested stainless steel powders and some of the used tools

In Figure 33 the bottles of the coated and uncoated 316L stainless steel [Baker97] are displayed with the Poly Acrilic Acid (PAA) used as the binder.

Case 2: rapid tooling, 3DP of alumina powders

The best line

Table XII - Main data and the range of parameters for the “perfect line”

Powder composition (% weight)	Drops	Powder bed
	Spacing: 3 - 28 µm	Speed: 10 mm/s
80% 20 µm spherical coated with 0.3 - 7% Darvan C®	Frequency: 0 - 1.5 kHz	Temperature: room - 180 °C
	Travel: 1 - 8 mm	Manual spreading
20% 2.5 µm	Speed: 10 - 15 m/s	Roll counter-rotating
	Volume: 0.7 - 1.4 * 10^{-3} mm^3	Non pressing / Tapping
	Diameter: 55 - 70 µm	
	Primitive ball: 90 - 140 µm	

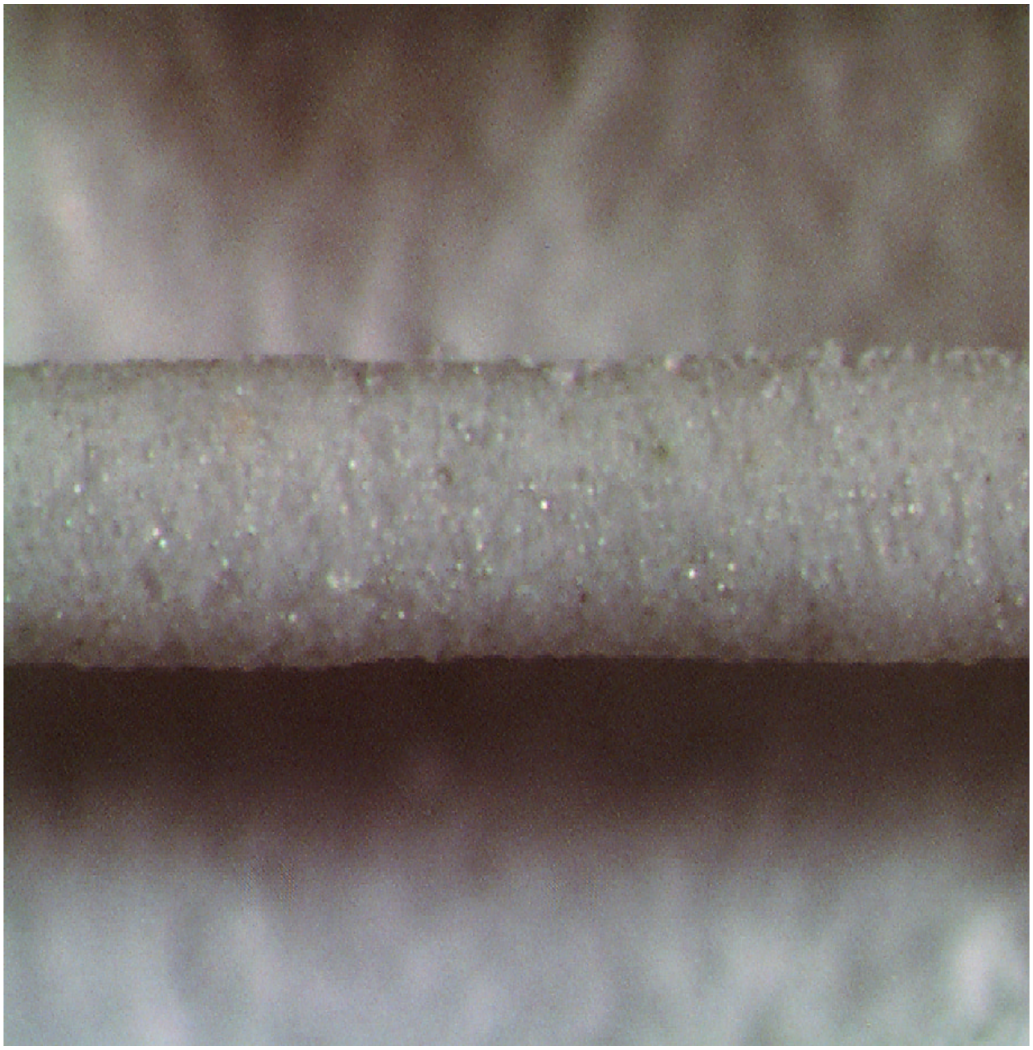

Figure 34 - The "perfect line" we have been looking for

Chapter XII.

THE PROPOSED THEORETICAL MODEL

Introduction

In this chapter, the main phenomena occurring in the primitive line formation are described. The model is deducted by indirect observation doing experiments in different changing conditions and evaluating the effects of changes. Understanding what is going on was a primary task in this study, because it represents the only way to optimize the process, have repeatable conditions, and overcome undesired effects.

The described model has only been experimentally validated by numerous tests but it requires direct observations to be absolute. Pictures are available to describe the tested conditions. The impact station with modifications[6] could be used to collect high-speed pictures. This theoretical model is probably not complete, because not all the possible conditions have been investigated. The conditions that have a practical interest have been tested and additional specific tests for doubtful situations have also been carried out.

The model at its present state is able to answer to similar situations to those occurred for its creation. For estimation purposes, it has validity until the same main physical phenomena are involved. Many issues have been answered after the final result has been achieved and verified. Until then, the incomplete model had a fair predicting power.

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[6] One of the problems with the impact observation station is the printhead dimension that would not allow a top view of the bed (when printing from a distance of about 1-10 mm) because the liquid reservoir is much wider than the nozzles plate. The camera should be inclined thus reducing the field of view. Mirrors or optic fibres would be necessary to overcome this visibility problem.

The biggest problem in understanding the line formation mechanism is however the visibility of the line within the powder bed.

Numerous tests have been carried out to assess the effect of the size distribution on the quality of a line.

A different approach to optimize the process

An alternate approach is to define a plan of experiments determining the main variables with a Design of Experiment (DOE) method and exhaustively test all conditions. In addition to be a much bigger work, for the numerous variables involved, the positive results would not be of much use when changing only one variable. 3DP is a complex, non-linear process involving many different phenomena and changing one variable require a definition of a new plan of experiments.

A mathematical model of the binder-powder interaction

Its implementation and use to predict the surface finish of lines in a specific condition require the measurement of all the physical and chemical properties because each of them may have a strong effect on the results. So it would not be practically useful because of the large experimental work required associated with its use.

On the opposite, assuming that all the parameters under control to avoid the measurements, the only use of a mathematical model would be the analysis of macro-geometric properties, such as the line size prediction or the penetration depth (like in [Fan95]), which is state of the art.

Details on the drop impact and on the line formation from [Fan95] and [Straube00]

Many phenomena involved in the binder drop-powder interaction have been dealt with by [Straube00] and [Fan95], using the droplet impact station. However, only what is visible by a camera could be investigated. Most observations have been confirmed in present study and they are reported for completeness.

[Fan95] only analyzed the impact of a single drop and mentioned the problem of crater formation and powder ejection, the liquid powder aggregate is formed simultaneously. In 1 ms all is done.

A distance of a few μm between drop and bed was observed [Fan95].

From [Straube00]. Drops take 10 μs to penetrate. There is more liquid in the centre and a successive migration for capillary. After 50 μs, starts the separation from surrounding powder, helped by the impact. After 200 μs the line has its final dimension. It is dry in 20 sec. [Straube00] did not provide an explanation for the line separation. According to this model it is due to the line contraction for rearranging.

Regarding lines, [Straube00] observed that: the mixture is pushed forth so drops do not fall in dry powder. The final line penetration is achieved 3-400 μs after the impact. On top of line is pure liquid and ejected particles impact on it. The trench is wider after 8-1400 ms for the ejection. In 3 ms all finishes. In up to 1 min the line is dry.

This "long" time could be useful for the mating of subsequent lines, for a better interaction and possibly a smoother rearrangement. These phenomena still need to be studied. The amount of ejected powder should also depend on the cohesive strength, so I assume that it decreases in the presence of moisture.

The main physical phenomena involved in the line formation

The following physical properties and phenomena have an influence on the interaction of a liquid and a powder. Their significance is known, but it is reported here for completeness, adapted to current case:

- to give a better feeling of why certain things happen;
- as a memorandum for people investigating the process.

Table XIII - The main phenomena and the effects of the physical and chemical properties involved in the line formation

property or phenomenon	definition and examples
density	the powder density influences the movement of grains and the interaction between the line and the powder below it for the

	force of gravity. The binder density influences the line weight too
surface tension	is the force between the binder molecules. It is higher for very polarized molecules. It represents the ability to make larger drops (or bubbles). It also represents the ability for small unit of liquid to make round surfaces (e.g. spherical or cylindrical) in order to minimize the surface energy. It directly affects capillary
capillary	is the ability to penetrate among grains. It is higher for water than colloidal silica in ethylene glycol. Considering the short time for the line formation, it can be probably neglected and instead of a penetration of the liquid in the bed we could talk of powder absorption in the liquid
viscosity	is the friction between the liquid molecules, and it represents the ability to move within the small spaces among grains
surface energy	is the polarisation of the surface. It represents the tendency to attract or be attracted by the binder molecules if they have an opposite sign and then the ability to engulf a grain of powder
surface energy (small powder)	if the powder surface is charged and the grains are sufficiently small, they tend to repel to each other. It typically occurs with 1 μm grains in a liquid. This is very useful according to the theory of the grains mobility (page 87) in a mixture of large and small size particles, because the small move very fast during the line formation and tend to assume the optimal position by filling all the spaces left empty
electrostatic force	it can be relevant for small powders
presence of humidity	this is critical especially for small powders and in general for all powders. It causes the formation of clumps, which are very

	undesirable. Heating the powder can reduce it for a short time and IF the environment humidity is low
dynamic pressure	the effect of the drop speed on the grain. This is the more relevant phenomenon at the impact. After that, it goes to zero
Laplace pressure	

The proposed theory

Alumina has a good wetting ability both with water or colloidal silica in ethylene glycol. This means that when a grain of powder comes in touch with a drop of water it is immediately engulfed. This effect is strongly amplified by the relative speed at the impact of a drop with the power bed.

A proof that the capillary penetration of the liquid observed by [Straube00], which make new drop fall in a liquid mixture, is positive is also given by the line quality improvement achieved reducing the drop spacing. The lower the drop spacing, the higher the superposition of drops, which make the difference between falling in a more or less liquid mixture.

In the first phase [Straube00] a drop penetrates into the bed engulfing more and more grains. Doing so its volume increases. At the same time, the powder reduces its density for the compression of new grains being engulfed.

With the addition of subsequent drops a line is formed. Most grains are engulfed from below the line.

While the line goes deeper in the bed, it starts increasing its width and creating a groove. The transverse section of the groove is a trapeze: the upper size is equal to the drop size and the bottom size is equal to the line diameter. In most cases, the cohesive force of grains make the bed unspoiled by these movements, so the internal surfaces of the grooves are usually even. When the line is formed it starts contraction and continue to penetrate in the bed absorbing grains from the bottom.

Some grains may fall from the groove sides. If the grains are free from each other, the powder bed remains unspoiled by these movements, and the internal surfaces of the grooves are smooth.

In the case of the multi-pass, if more drops are added to a line in successive passes, the line diameter increases for the liquid addition and because the powder absorption phenomenon starts again. It can be observed that the line becomes larger than the groove that contains it, because the groove size is determined by the size ofthe drop-powder mixture in the first pass. In the second (and successive) pass the drop does not encounter any loose powder before reaching the line so the groove borders remain untouched.

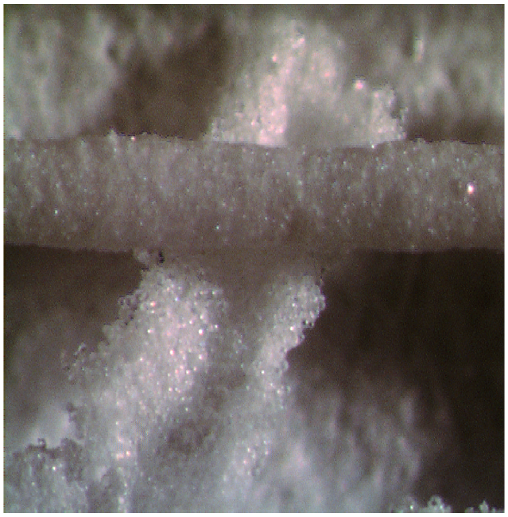

Figure 35 - A line and a compact bed part showing its negative

The line quality is mostly determined by what happens after the initial formation. At this stage, the liquid-powder mixture lays on a powder bed and still touches the walls of the groove containing it. The powder wetting property make all the grains in the bed touched by the liquid be engulfed in the line, **IF** the force is sufficient. In this situation, on each grain two opposing forces act: one is the attraction inside the liquid, the other is the friction by the bed.

In Figure 35 the smooth surface of a line and the irregular internal surface of a bed part that was outside it are displayed. This quality difference shows the rearrangement of the powder mixture and the separation between line and bed.

According to the position of the grain with respect to the line, on a side, or below it, the **gravity** may also contribute. In particular, for higher density materials than alumina, such as metals, gravity is probably more important not only helping grains drop into the line, but also to engulf grains from the bottom for the higher weight of the formed line.

After all grains touching the line sides have been engulfed, they are rearranged again in order to achieve the minimum volume and then the maximum density. If some grains cannot be engulfed, they remain in an unstable condition and give **WORST** line quality. If they can move in, the line becomes smoother after compression. This phenomenon is stopped when, after compression, the line is not touching anymore the groove sides, but only its bottom. For this reason, better lines are neatly separated from the bed and the powder removal through compressed air is easier. In the other case, grains included in the line are also connected to the unbound bed powder, so removal is more difficult.

The axial movement of grains

One drawback of the multi-pass method is the presence or the enhancement of the defect "size undulation", a symmetrical repeated line size variation. It is probably due to an amplification of the axial displacement of grains helped by the presence of the liquid addition before it dries. The presence of this axial displacement is supposed by a simple theoretical consideration. If we think to a radial displacement of grains only due to the line compression during formation, then we should conclude that the undulation is only due to an irregular powder distribution. causing a narrower line for the absence of some grains. Of course this is always possible, but it has a very low probability, while this phenomenon is very widespread and it is enhanced on lines obtained in a double-pass with respect to those obtained in single pass within the same bed.

What causes the resultant of forces acting on grains to move axially is very difficult to say. It is probably derived by the subsequent addition of drops to the line.

However a small axial movement of grains is always possible because during the line contraction the lower energy status can be achieved by moving grains in a direction that is not necessarily radial.

The formation of a line by contraction and smoothing operated by the liquid is evident. There is a direct observation related to these theoretical considerations. The presence of small and large bubbles can be considered as a case limit of very amplified undulation. The fact that they share the same nature and that they are due to similar causes is confirmed by their coexistence in all the observed beds. Bubbles can be of different types:

4. very large, symmetrical increase or reduction of the line size, starting from half the line size or
5. line interruption with a spheroid end or
6. a separated bubble.

In both cases the axial displacement of grains has been clearly observed through the shape of grooves containing lines.

Chapter XIII.

CONCLUDING REMARKS

Conclusions

Obtaining "good primitive lines" is a necessary step for the process optimization, to achieve better surface finish and geometrical tolerances. With some new material system, just obtaining a line is sufficient, but this is not the case with alumina powders that have been printed since the beginning of the 3DP technology.

In this project the main parameters and variables to improve the quality of lines have been pointed out. From the extensive data collection coming from the numerous experiments carriedout a theoretical model has been deducted. In addition to all the necessary setup and debugging tests, 56 beds have been printed and documented in complete file reports with an average of 30 lines/rings each. A total of 40 beds were still readily available at the end of the project, more than 1300 primitive lines. Over 50 meters of solid, clean lines, with different parameters and printing conditions. Lines and beds are documented in 180 pictures at the optical microscope and 260 at the ESEM.

3DP is a complex process involving many different physical phenomena. Some of them are more relevant than others, but to achieve the best results all of them must be under control. The more relevant parameters and their effects are also listed in this report.

It has been shown that the right powder composition, surface coating, and drop spacing give the most relevant effects and their values are given in this report for the examined material system. But also less controllable or quantitative factors like spreading or the presence of humidity and clots have a strong influence on results.

The proposed theoretical model and the definition and the classification of line defects are a key for understanding the reason of unsuccessful results and to correct them.

The multi-pass method has been applied for the first time and its use is proposed here. It allows improving the line quality by printing it again. The only drawback is the increased line width. In no case worst lines have been obtained. It can also be used to flatten lines on certain powder mixtures and in certain conditions, which is useful on the last layer.

This report also contains useful (I would say necessary for a novice) practical methods to conduct experiments and measures about the examined material systems and the hardware used.

Looking for the perfect layer and for the perfect final part

A methodology, which has been successfully applied to two different cases was described. It includes an analysis of the process and the use of standard and new techniques to improve the quality of line.

This approach can be extended and applied to primitive layers, to the final object and to new material systems.

Future developments

Although this project can be considered achieved in the sense that a good local optimum point as been found, this is probably only the starting point for further investigations to understand more about the process in order to have a better control in all situations.

The drop speed could not be changed with the used printhead. However an interesting test would be inclining the printhead with respect to the bed to assess different effects:

- mainly a reduction of the speed component perpendicular to the powder bed;
- a different angle with respect to the force of gravity;
- a different groove depth and shape in the powder ejection;
- the more turbulent (revolving) powder motion and torsion of the formed line.

There was not much time left to understand the effects of the different physical and chemical properties of this or other material systems. For instance **changing the**

binder composition. In this project, a 50% vol. solution has been used. The percentage of water with colloidal silica in ethylene glycol could be changed to enhance or reduce the effects of properties such as viscosity, wettability and investigate/verify their effect according to the proposed model.

The effect of the powder density could be evaluated using a powder of different material with the same size distribution, coated to have a similar surface behavior.

At present, a new 3DP machine is under study. It has, among others, the following features as opposed to the Alpha Machine: it can print slurries, it has a vector motion of the printhead, andit uses a DoD printhead. A new piezo nozzle is also under study as an evolution of the Siemens PT 88 S printhead. With this printhead the maximum frequency of 3 kHz can be obtained as opposed to the 1.5 available with the printhead used in this project. The whole range between 10 and 1,500 Hz was explored in this project and no relevant effect has been noticed. It is possible that some effects of the drop frequency are available in the 1.5-3 kHz range, so it should be investigated if adopting the new printhead on the new machine with the material system described in this project.

The multi-pass method is one of the most promising techniques developed in this project. An important aspect needs further investigation: printing the binder on the final surface in order to flatten lines and produce more even surfaces. This analysis of layer behavior goes beyond the purpose of this project that focuses on lines, but probably the good results achieved with lines can be extended to layers.

LIST OF SYMBOLS, UNITS OF MEASURE AND ABBREVIATIONS

D_s. Drop spacing, the distance between the two drop centers, usually [μm]

D_V. Drop Volume [μm^3]

f. frequency of drops [Hz], for thermal or bubble jet printheads it can be up to about 1.5 [kHz]

f_r. flow rate of the binder [pl/s]

I_S. Impact Speed or drop speed [m/s]

L_s. Line spacing, the distance between the two line axes, usually [μm]

L_w. Line width, the diameter of the average cylinder containing a line, usually [μm]

S_f. fast axis Speed, [μm/s], [mm/s]

GLOSSARY

-#. e.g. -10, -15, -28. Read minus and the number. It represents the size distribution of a given powder. It means that it contains particles smaller or equal than # μm. If the minus sign is not present, all the particles should be the same size # μm. A "<" sign can also be found instead of a "-"

3DLine/3DRing/Alpha Machine. Respectively, short names of the two configurations of the experimental set-up developed in this project for printing straight lines or rings and the first machine developed, currently available at the 3DP Lab. 3DLine and 3DRing are the acronyms for 3DPrinting Ring and Line machine.

3DP. Three Dimensional Printing is a process for the rapid fabrication of three-dimensional parts directly from computer models. A solid object is created by printing a sequence of two dimensional layers. The creation of each layer involves the spreading of a thin layer of powdered material followed by the selective joining of powder in the layer by printing binder material.

CJ. Continuous Jet. An inkjet printing technique based on the deviation of a continuous flow of drops to the powder bed or to a catcher to recycle the unused binder. It is actually adopted on the Alpha Machine in a multiple (eight) nozzle printhead based on the piezo effect.

DoD. Drop on Demand. The principle of inkjet printing with thermal (or bubble) and piezo printheads as opposed to CJ. Drops are created by generating a suitable wave. In this project, a DoD, commercial, thermal printhead was used, printing from one nozzle at a time.

Fast/Slow Axis. The main axes of a 3DP machine. The fast axis is used to print primitive lines. The slow axis determine the line spacing.

Large/Small Powder. To be intended as average large/small grain size powder. In this project 10-30 μm powders have been used as large powders and 1 to 5 μm have been used as small powders. The size distribution is indicated in this report when available.

SEM. Scanning Electron Microscope. The microscope available in bldg. 13 at the MIT can also work with water vapor. This means that also non-metals are visible without additional treatments. In particular, for alumina powders, no gold or carbon plating[7] is required.

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[7] For this reason the slurry-based 3DP technology has been developed.

[7] This procedure is available at bldg. 12.

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Appendix A

COMPATIBILITY CHART FOR THE PRINTHEAD HP51626A

From http://www.hp.com/cposupport/printers/support_doc/bpa00585.html

The HP 51626A printhead cartridge (Black, 40 ml) is used with:

HP DeskJet Printers (*)

Plus, 400, 400L, 420, 420C, 500, 500C, 505K (Korea), 510 (Europe), HP DeskJet 520 (Europe), 540, 550, 560

HP DeskWriter Printers (*)

520, 540C, 550C, 560C

HP DesignJet Printers

200, 220, 600

HP OfficeJet

LX, 300, 330, 350

HP FAX

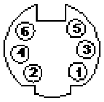
200, 300, 310, 700, 750, 900, 950

(*) The HP 51626G cartridge model (Black, 20 ml) is only working on HP DeskJet and DeskWriter Printers.

Appendix B

PS/2 KEYBOARD OR MOUSE PINOUT

From http://www.nti1.com/technote.html



Mating face of 6 pin miniDIN female

PIN#	SIGNAL	PIN#	SIGNAL
1	**DATA**	**4**	**+5**
2	**NC**	**5**	**CLOCK**
3	**GND**	**6**	**NC**

The PS/2 port on the PC is connected to the 3DLine/Ring Machine by a disassembled mouse. It is used

1. to feed the external electronic circuit that converts the signal from the parallel port of the PC into power to drive the slow axis motor: pins # 3 and 4, and
2. to input the "end of a line/ring" signal (interpreted as a right mouse click) from the Machine switch connected in parallel to the disassembled mouse.

Appendix C

THE POWDERS USED IN EXPERIMENTS

Main features, laboratory and commercial references

Alunabeads (Japan) CB-A20S, Lot BGU
Aspect 1 kg bottle

Alunabeads (Japan) CB-A01, Lot MKP
Aspect 100 g bag

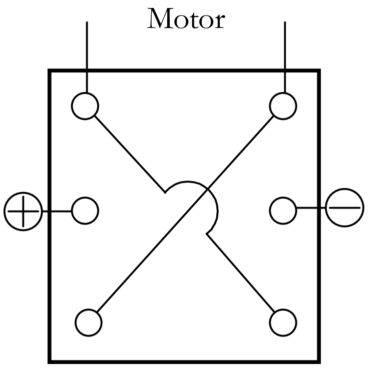
Data sheets of all the Alunabeads powders from the manufacturer (including the A30S, A02, A10) are available at the 3DP Lab.

It was not possible to have information on the Electro Abrasives powders marked (by pern) #3 and #5 because the manufacturers was not available anymore in Buffalo (NY).

Some of the stainless steel powders are displayed in Figure 33 of page 97.

Figure 36 - Photo family of the tested alumina powders

FORWARD/BACKWARD SWITCH



Appendix E

THE ENVIRONMENTAL SEM

Introduction

A Scanning Electron Microscope uses an electron beam to image. Since the wavelength of an electron beam is shorter than that of a light beam, the SEM is able to resolve much greater detail than an optical microscope. The resolution limit of modern SEM is on the order of tens of nanometers.

The Environmental Scanning Electron Microscope (ESEM) has the ability to image samples without the need for a very high vacuum. This allows the imaging of samples in a low-pressure gas environment. More importantly, since the gas (typically water vapor) is weakly conductive, the presence of the gas environment permits the imaging of non-conducting samples without the need for gold- or carbon- coating.

An optional attachment to the SEM permits a rough elemental analysis of the sample under study.

Discussion on high and low vacuum

High vacuum mode is the traditional operating mode of the SEM. It provides the most well understood image features, the highest resolutions (but the resolution of wet mode is not bad), and the best X-ray analysis. On the other hand, samples which are not electrically conductive will charge up, deflecting the secondary (and in severe cases, the primary) electrons, ruining the image. Insulating samples can be coated with a thin conductive layer of, for example, gold, but this has numerous disadvantages. Samples which are incompatible with a high vacuum (undried biological samples, for example) cannot be examined in high vacuum mode.

By introducing a gas into the chamber, many of the problems of high vacuum operation can be overcome. The primary electron beam ionizes some of the gas, creating a plasma of ions and electrons which, except in severe case, can control any charging that might build up. In addition, because the system can cope with a "poor" vacuum, samples such as untreated biological specimens, which outgas a lot, can be examined readily (though, if they are drying as they are examined, they will change and may be mechanically unstable). It is even possible, with the provision of a cool stage, to condense water on the sample, but we don't have that accessory. There are, of course, disadvantages of wet mode. The primary electron beam is partially scattered by the gas in the chamber, leading to a loss in image contrast and a loss in resolution during x-ray analysis. The pumping apertures that must be installed in the column lead to a restriction in the field of view of the sample at low magnification (the main difficulty that this creates is finding one's way around the sample). The conventional secondary detectors do not work, so special detectors must be installed for wet mode. We do not have a good backscatter detector for wet mode operation.

References

More information on the product can be found here: http://www.feic.com/products/xl30feg.htm

The ESEM page (with tutorial and booking) at the MIT can be found at: http://prism.mit.edu