

Laser Sintering with Plastics

Technology, Processes, and Materials





Schmid Laser Sintering with Plastics

Schmid

Laser Sintering with Plastics

Technology, Processes, and Materials

HANSER Hanser Publications, Cincinnati

Hanser Publishers, Munich

The Author:

Dr. Manfred Schmid, Inspire AG, CH-9014 St. Gallen

Distributed in the Americas by: Hanser Publications 6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA Fax: (513) 527-8801 Phone: (513) 527-8977 www.hanserpublications.com

Distributed in all other countries by: Carl Hanser Verlag Postfach 86 04 20, 81631 München, Germany Fax: +49 (89) 98 48 09 www.hanser-fachbuch.de

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone. While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

The final determination of the suitability of any information for the use contemplated for a given application remains the sole responsibility of the user.

Cataloging-in-Publication Data is on file with the Library of Congress

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich 2018 Editor: Dr. Julia Diaz Luque Production Management: Jörg Strohbach Coverconcept: Marc Müller-Bremer, www.rebranding.de, München Coverdesign: Stephan Rönigk Cover image: Inspire AG Typesetting: Kösel Media GmbH, Krugzell Printed and bound by Druckerei Hubert & Co GmbH und Co KG BuchPartner, Göttingen

Printed in Germany

ISBN: 978-1-56990-683-5 E-Book ISBN: 978-1-56990-684-2

Foreword

The history of additive manufacturing might seem to be very short, but in reality the technology is more than a hundred years old. The first patent application was in 1882 by J.E. Blanther, who registered a method for producing topographical contour maps by cutting was sheets, which were then stacked.

This is an amazing fact: layer-by-layer work processes are currently experiencing a huge amount of hype that was not triggered by the development of new basic technologies. Rather, the reason for this is that essential patents have expired, making it possible to recreate for example a melt deposition method using the simplest means, which can be used for the generation of three-dimensional bodies. However, this hype managed to develop, in a very short time, an immense momentum. The user centralization and the new degrees of freedom offered by the technologies coincide with the present boom of DIY (do-it-yourself) culture, so it is not surprising that "fabbers¹" and "3D printing selfies" are in high demand.

Conversely, various new technologies were developed over the entire process chain as well. During my studies in the early 2000s, when I dealt with the topic for the first time, the importance of layer manufacturing was only high in the area of prototyping. The technologies have not changed radically since then, but nowadays the market for custom products and small production runs has increased massively in many industries. Both established machine manufacturers and many innovative startups have joined this field. The additive manufacturing process has found a previously unimagined extent of application, from the production of individual toys to high-power components for powertrains. In the future, different scenarios for production are conceivable, and decentralized production "on demand" is tangible. This generates a possible area of conflict from high technological expectations, risks, and potentials. A realistic estimation should not be based solely on the enthusiasm that is noticeable after seeing the first additive manufacturing process and having the generated part in ones hand. Independent research on the topic is therefore essential.

¹ "Fabber": Short for digital fabricator. A machine that makes arbitrary three-dimensional objects automatically from raw materials and digital data.

BMW AG ordered the first SLA system in 1989. Thus, BMW AG was the first customer of a today world-recognized and leading company of laser sintering systems. Over the years, from the first model-making facilities, a center of competence within the *Research and Innovation Center* (FIZ) evolved, in which various types of practical and basic research are carried out today. In addition to high-quality prototypes for testing and validation of transportation vehicles, materials and processes are being developed, making it possible to realize the potential of layer-by-layer construction. For example, employees working in automotive production are individually equipped with personalized assembly aids to increase ergonomics and performance in assembly lines.

In this case, the focus of the discussion will be less on the 3D printing processes mentioned in the media, but rather on the highly complex manufacturing machines on which the production is to take place in the future. One such technology is laser sintering (LS), a laser-based unpressurized manufacturing process. However, the coincidence with a "real" sintering process is solely that the generated part cross section will be held near its melting temperature for a long residence time. This is the core process of laser sintering, which has been examined in diverse ways and is still subject of intensive further research.

As part of my own PhD thesis, I dealt with the time and temperature dependence of the two-phase region, in which melt and solid are present and sharply demarcated. I had thus the chance to enter one of the many interdisciplinary fields of research on additive manufacturing, and am still excited about this topic. Anyone who intends to study or work with laser sintering will not be able to find a lot about such a specialized topic in most of the general books on 3D printing and additive manufacturing. However, as powder-bed-based technologies are established as one of the major additive manufacturing processes, it is essential to present the results of basic research and transfer them to practical use in order to create, for example, as a service provider, viable high-quality parts. The purpose of this book by Manfred Schmid, one of the recognized specialists in laser sintering, is precisely to give this depth of field without losing sight of the benefits for the user.

Dr.-Ing. Dominik Rietzel May 2015

About the Author

Dr. Manfred Schmid began his professional career as an apprentice laboratory assistant at *Metzeler Kautschuk AG* in Munich, Germany. After graduation, he studied chemistry at the University of Bayreuth (Germany), where he obtained a PhD degree in macromolecular chemistry. He worked on liquid-crystalline polyurethanes under the guidance of Prof. Dr. C. D. Eisenbach.



After completing his studies, he moved to Switzerland, where he worked for 17 years in industry in various positions in the areas of polymer research and produc-

tion as well as material testing and polymer analysis. Polyamides and biopolymers were the focus of these different industry positions.

Since 2008, he leads the research in laser sintering (LS) at *Inspire AG*, the Swiss Competence Center for Manufacturing Techniques. *Inspire AG* acts as a transfer institute between universities and the Swiss machine, electro, and metal (MEM) industries.

The focus of his current activities is in the area of new polymer systems for the LS process, the analytical evaluation of such materials, and the qualitative and quantitative improvement of the LS process. He supervises several employees and research projects in this field.

As a guest lecturer, he occasionally lectures on materials science of polymers, manufacturing processes of polymers, and 3D printing at NTB Buchs (Interstate University for Applied Science, Switzerland) and in the University of Applied Science St. Gallen, Switzerland.

The idea for this book emerged from several internal training courses on additive manufacturing conducted at *Inspire AG* for large industrial companies.

Contents

For	eword	V
Abo	ut the Author	VII
1	Introduction	1
1.1	Manufacturing Technology	1
1.2	Additive Manufacturing	2
	1.2.1 Areas of Application/Technology Driver	3
	1.2.2 Polymer-Based AM Method	5
	1.2.3 Technology Maturation	7
	1.2.4 Laser Sintering (LS)	9
1.3	References of Chapter 1	11
2	LS Technology	13
2.1	Machine Technology	15
	2.1.1 Machine Configuration	15
	2.1.2 Temperature Control	17
	2.1.2.1 Heat Sources	18
	2.1.2.2 Surface Temperature in the Build Cavity	19
	2.1.2.3 Laser Energy Input, Andrew Number (A_n)	20
	2.1.3 Powder Feed	22
	2.1.3.1 Powder Supply	22
	2.1.3.2 Powder Application	24
	2.1.4 Optical Components	28
2.2	Machine Market	29
	2.2.1 3D Systems (USA)	29
	2.2.2 Electro Optical Systems – EOS (Germany)	31
	2.2.3 Aspect (Japan)	32
	2.2.4 Farsoon (China)	33

		Comparison of Commercial LS Machines	34 35
		Other Machinery	
2.3	Refere	ences of Chapter 2	37
3	LS P	rocess	39
3.1	Proce	ess Chain	39
	3.1.1	Powder Preparation	40
	3.1.2		42
	3.1.3	Build Process	44
		3.1.3.1 Heating	44
		3.1.3.2 Process Cycle	44
		3.1.3.3 Parts and Build Chamber Parameters	48
		3.1.3.4 Strategy of Part Irradiation	49
		3.1.3.5 Cool Down and Part Extraction	51
	3.1.4	Process Errors	53
		3.1.4.1 Deformation of the Part	53
		3.1.4.2 Surface Defects: Orange Peel	55
		3.1.4.3 Other Process Errors	56
3.2	Quali	ty Assurance	57
	3.2.1	General Quality Actions	57
	3.2.2	Test and Comparison Parts	59
	3.2.3	Quality Costs	61
	3.2.4	PPM Concept (EOS)	61
	3.2.5	State of Standardization	62
3.3	Refere	ences of Chapter 3	64
4	LS M	aterials: Polymer Properties	65
4.1		ners	65
т. 1	-	Polymerization	66
		Chemical Structure (Morphology)	68
		Thermal Behavior	69
		Polymer Processing	70
		Viscosity and Molecular Weight	71
4.2		Properties of LS Polymers	73
	4.2.1		74
		4.2.1.1 Crystallization and Melting (Sintering Window)	75
		4.2.1.2 Heat Capacity (c_p) and Enthalpies $(\Delta H_k, \Delta H_m)$	80
		4.2.1.3 Thermal Conductivity and Heat Radiation	80
		4.2.1.4 Modeling the Processes in the Sintering Window	82

	4.2.2	Rheology of the Polymer Melt	83
		4.2.2.1 Melt Viscosity	84
		4.2.2.2 Surface Tension	86
	4.2.3	Optical Properties	87
		4.2.3.1 Absorption	88
		4.2.3.2 Transmission and (Diffuse) Reflection	90
	4.2.4	Particles and Powder	91
		4.2.4.1 Powder Rheology	92
		4.2.4.2 Particle Size Distribution	95
		4.2.4.3 Powder Density	96
4.3	Refer	ences of Chapter 4	98
5	LS M	aterials: Polymer Powders	101
5.1	Produ	ction of LS Powders	101
	5.1.1		102
	5.1.2	Precipitation from Solutions	103
	5.1.3	Milling and Mechanical Grinding	104
	5.1.4	Coextrusion	105
	5.1.5	Overview: Production of LS Powders	106
	5.1.6	Other Powder Manufacturing Processes	107
		5.1.6.1 Spray Drying	107
		5.1.6.2 Drop Extrusion	108
		5.1.6.3 Melt Spinning	108
		5.1.6.4 RESS with Supercritical Gases	109
5.2	Evalu	ation of the Powder State	109
	5.2.1	Thermal Analysis	110
		5.2.1.1 Differential Scanning Calorimetry (DSC)	110
		5.2.1.2 Thermogravimetry (TGA)	111
	5.2.2	Melt Viscosity	112
		5.2.2.1 Melt Flow Index (MVR/MFI Measurements)	112
		5.2.2.2 Molecular Weight and Residual Monomer Content	114
	5.2.3	Particle Shape and Powder Distribution	115
		5.2.3.1 Shape and Surface	116
		5.2.3.2 Volume and Number Distribution	117
	5.2.4	Free-Flowing Behavior of Powders	118
		5.2.4.1 Hausner Factor (HF)	120
		5.2.4.2 Revolution Powder Analysis	122
5.3	Refer	ences of Chapter 5	123

6	LS Materials: Commercial Materials	125
6.1	Polyamide (Nylon)	129
	6.1.1 Polyamide 12 (PA 12)	130
	6.1.1.1 Powder Distribution and Particles	131
	6.1.1.2 Thermal Properties	134
	6.1.1.3 Crystal Structure	139
	6.1.1.4 Molecular Weight and Post-Condensation	141
	6.1.1.5 Powder Aging	145
	6.1.1.6 Property Combination of PA 12	147
	6.1.2 Polyamide 11 (PA 11)	148
	6.1.3 Comparison of PA 12 and PA 11	149
	6.1.4 PA 12 and PA 11 Compounds	151
	6.1.5 Polyamide 6 (PA 6)	152
6.2	Other LS Polymers	153
	6.2.1 Polyether Ketone (PEK)	153
	6.2.2 Flame Retardant Materials	154
	6.2.3 Polyolefins	155
	6.2.3.1 Polyethylene (PE) and Polypropylene (PP)	155
	6.2.3.2 Polystyrene (PS)	156
	6.2.4 Elastomeric Materials	156
	6.2.4.1 Thermoplastic Polyurethane (TPU)	157
	6.2.4.2 Thermoplastic Elastomers (TPE)	157
6.3	References of Chapter 6	158
7	LS Parts	161
7.1	Part Properties	162
/.1	7.1.1 Mechanical Properties	162
	7.1.1 Mechanical Properties	162
	7.1.1.2 LS Build Parameters	164
	7.1.1.3 Part Density	165
	7.1.1.4 Degree of Particle Melt (DoPM)	168
	7.1.1.5 Anisotropy of the Part Properties	171
	7.1.1.6 Long-Term Stability	174
	7.1.2 Part Surfaces	174
	7.1.2.1 Influence Parameters	174
	7.1.2.2 Roughness Determination	176
	7.1.2.3 Surface Finishing	177
	7.1.2.4 Finishing	178
72	Applications and Examples	181
		101
	7.2.1 AM-Compatible Design	181

Ind	ex	195
8	LS Materials Table	191
7.3	References of Chapter 7	189
	7.2.6 AM Business Models and Outlook	186
	7.2.5 Customization	186
	7.2.4 Reduction of Part Lists	185
	7.2.3 Functional Integration	183
	7.2.2 Model/Prototype Construction	182

Introduction

1.1 Manufacturing Technology

Production or manufacturing is a process by which products (parts, goods, or merchandise) are generated. The products are obtained through operations on other parts (semi-finished) or created from other materials. Production can be done either manually or by machine.

The different manufacturing technologies are discussed within the field of manufacturing according to DIN 8580, in which the following classifications of manufacturing processes (processes for the production of certain geometric solids) are identified:

- Primary shaping: A solid body is formed from shapeless materials (liquid, powdery, plastic); the cohesion is provided by, for example, casting, sintering, kilning, or curing
- Forming: Deformation of a body by malleable changes without changes in the amount of material (for example, bending, drawing, stamping, or rolling)
- Joining: Previously separate workpieces are converted into a solid compound (for example, gluing, welding, or brazing)
- **Machining:** Change in the shape of a solid body; the cohesion is eliminated locally (typically by a removing process such as grinding or milling)
- **Coating:** Surface treatments of all kinds (for example, painting, chrome plating, etc.)
- Change of material properties: Conversion by post-treatment (for example, hardening)

The various technologies considered as additive manufacturing processes developed during the past three decades are classified as primary shaping processes (see, for example, ISO 17296-2:2015). Hereby powder, melt, or liquids are transformed into novel components using different energy sources or by chemical reactions. A solid body is formed from previously formless substances. The final properties of the part therefore only arise during the manufacture; this means that, besides the material, also the build parameters determine the final part properties.

1.2 Additive Manufacturing

Additive manufacturing processes always take place layer by layer; thus they are sometimes called layer manufacturing technologies. In ASTM F2792-12a, additive manufacturing (AM) is defined as:

Additive manufacturing (AM), n:

Processes for joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing fabrication methodologies.

By this ASTM definition, the layered structure of the objects is defined. The shape of the part is submitted in the form of electronic data recorded in the computer that controls the formation of the part directly (direct digital manufacturing). This is clearly different from subtractive machining methods.

In additive manufacturing it is common that, for the production of a part, the material is gradually joined only where the part should be built up. In contrast, in traditional subtractive methods, the material is removed (subtracted) from a semi-finished product by cutting techniques such as milling, drilling, and turning, to produce the desired part.

In additive manufacturing, due to the fact that the parts are created in layers during the build—that is, in two dimensions—the complexity of the part in the third dimension plays a secondary role during processing. Parts with virtually any 3D complexity can thus be built.

In general, humans have used the principle of additive manufacturing since prehistoric times, for putting material together only where it is really needed. Nearly every house is created additively. Building blocks are assembled in layers to form walls. A wall is formed where it is needed and at the end of the construction, previously empty space is surrounded with solid material.

Hardly anyone has the idea to fabricate a house from a previously manufactured concrete block with a hammer and a chisel. Nevertheless, there are several examples in history of buildings created with subtractive technologies. Figure 1.1 shows an attempt at that (World Heritage Site Petra, Jordan).

Additive manufacturing technologies have been known in the industry for a long time under the name of "rapid prototyping (RP)". Rapid prototyping was and is mainly used for modeling and product development in many industries in order to

obtain design samples and/or to achieve a reduction in the length of development cycles.

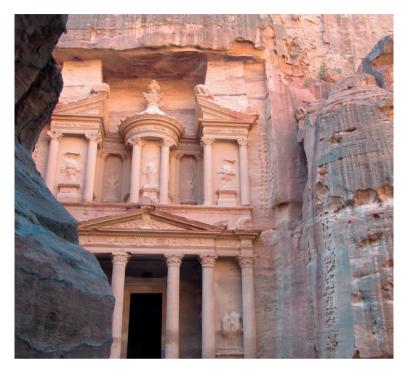


Figure 1.1 Construction of a building with subtractive technology [source: A. Strub]

Thus, what professionals have known for a long time has nowadays created a media hype known as "3D printing", putting the technology into the light of public perception. However, in the media, little differentiation is made, and creating a weapon by additive manufacturing appears in the same context as the production of artificial human organs. Whether the process works with metals, plastics, or ceramics is also largely ignored.

1.2.1 Areas of Application/Technology Driver

The different AM methods have the common characteristic that they do not require the use of a tool to provide the shape of the desired part. Layered tool-less forming provides many advantages, which particularly concern the following areas and are considered to be the main driver of AM technology:

- Economic fabrication of small production runs (batch sizes start with one part)
- Geometric freedom in design (free-form surfaces, undercuts, cavities)

4

- Components with integrated functions (hinges, joints, flexible units)
- Product personalization (medical, sports)
- Rapid product customization (shorter product cycles)
- Ecological aspects (lightweight, reduced material consumption)

Typical industries in which the advantages of additive manufacturing are very suitable and that can be targeted are the aerospace industry, the defense industry, the automotive industry, medical technology, electronics, furniture, jewelry, sports equipment, and tool and mold making.

Some already established business models (such as customized drilling guides for surgery, individual dental prosthetics, complex furniture bearings, new filter systems, robotic grippers) are evidence of the economic use of AM technology today. Where additive manufacturing economically beats traditional production methods is shown schematically in Figure 1.2.

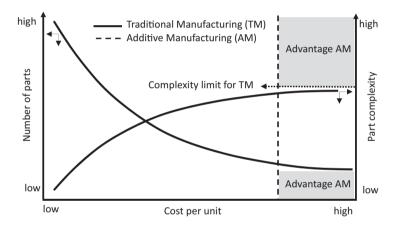


Figure 1.2 Cost per unit versus the number of parts and the complexity for traditional manufacturing methods (TM) and additive manufacturing (AM)

Established production technologies are often optimized for high part quantities to be produced with the lowest possible costs. Typically the costs per unit decrease significantly with the number of parts produced. At the same time, in traditional production technologies, the costs increase significantly with the complexity of the part. Usually, a limit of complexity is reached with traditional methods, which cannot be overcome easily or can only be implemented with exorbitantly high costs.

Herein can be found the advantages of additive manufacturing processes (see the highlighted areas in Figure 1.2). The unit cost is almost unchanged for small part quantities or parts with substantial complexity. To take advantage of these benefits, the design process must be changed from:

manufacturing driven design into functionality driven design!

This paradigm shift in part design affects the entire process chain for part production. In product development projects, the planned manufacturing process should already be integrated into the design process at the beginning of the project in order to take advantage of all the benefits that additive manufacturing can offer.

In the future, additive manufacturing will be integrated into the field of different production technologies and will be preferably used when small batches of highly complex parts must be produced.

Manufacturers should recognize the possibilities that additive manufacturing offers and should try to use it to their advantage. This requires that the company rethink many of their areas. In product design and fabrication, completely new approaches will result. Supply chains and business models will change significantly in the environment of AM. Mass production in low-wage countries will be rearranged into local, decentralized manufacturing of highly specific components. Logistics will shift from shipping parts to shipping electronic data.

Because additive technology is still in the early stages of development, there are still many obstacles to overcome. Besides the legal aspects that accompany digital production (for example, data security), there are still substantial problems, particularly in the plastic sector, to be solved.

1.2.2 Polymer-Based AM Method

Approximately 35 years ago, Chuck Hull's work on stereolithography began and finally led to the creation of the company 3D Systems, which today owns and further develops diverse additive technologies. The individual technologies are, in part, based on totally different principles of material cohesion, and they also use completely different initial materials [1].

In the field of plastics, with respect to material formation, chemical reactions (UV curing) are as common as thermally induced processes (softening, melting). Adhesion of individual particles using suitable binders (3D printing) has also been technologically implemented. Figure 1.3 shows a classification of additive processes that originate from plastics. This ordering is based on ISO 17296-2:2015 in terms of the material and process matrix.

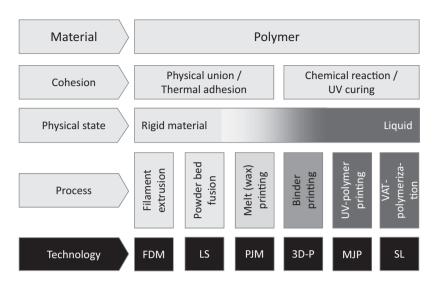


Figure 1.3 Characterization matrix for additive manufacturing processes with polymers as the raw material (in accordance with ISO 17296-2:2015)

With the data presented in Figure 1.3, technologies can be characterized as follows:

Filament extrusion (fused deposition modeling, FDM®)

In FDM[®], polymer filaments that are predominantly amorphous are heated and conducted through a heated nozzle to be glued in layers.

Laser sintering (LS)

By the introduction of energy, spatially resolved powder particles are fused together using a laser. By overlapping layers of powder, a three-dimensional body is produced.

Wax printing (PolyJet[®] modeling, PJM)

Melted wax passes through a print head (analogous to inkjet printing); the printed wax drops solidify when deposited on the substrate.

3D printing (3D-P)

A suitable binder is printed via a print head onto a powder substrate; the powder can be inorganic in nature (e.g., gypsum) or plastic, metal, and ceramic.

Inkjet UV printing (multijet printing, MJP)

UV-curable pre-polymers are deposited with a print head as small drops, which are spatially located and cured by a UV source attached to the print head.

Stereolithography (SL)

The desired layer information is introduced by the energy input of a UV laser in a bath of UV-curable pre-polymer. Where the laser hits the UV-sensitive mass, there is a chemically induced curing. The result is a part layer. Other methods not listed in the diagram of Figure 1.3, which are not included in the aforementioned ISO standard, but which also produce additive parts with plastics as starting materials, are:

■ Selective heat sintering (SHSTM)

Analogous to the LS method, but the energy input to melt the powder particles is not aimed to a point as with a laser, but rather over the whole powder bed using a thermal transfer print head (company: Blue Printer).

• ARBURG polymer freeforming (from German: ARBURG Kunststoff-Freiformen, AKF)

Through a piezo-controlled nozzle, molten polymer drops are spatially positioned and deposited; by three- or five-axis movement, the print head generates the complex part (company: ARBURG).

Absorbing ink printing (Multi Jet Fusion[®], MJF)

In a plastic powder bed, an IR-absorbing ink is printed. The subsequently applied IR lamp melts the powder in the printed areas (the market introduction of this process by the company Hewlett Packard (HP) was announced for 2017).

More information and a detailed description about the advantages and disadvantages of most of the methods mentioned above can be found in the general literature about 3D printing [2] [3]. A nearly complete list of all currently available 3D printers can be found on the Internet [4].

1.2.3 Technology Maturation

Due to the different technological approaches to the production of AM parts, it can be expected that the resulting products have very different properties. In Table 1.1, a qualitative evaluation of the processes in terms of component properties for various boundary conditions is made (according to [5]). From this, the predominant uses of parts produced with the different methods can be defined.

Process	FDM	LS	PJM	3D-P	MJP	SL
Principle	Filament extrusion	Powder bed fusion	Wax printing	Binder printing	UV-polymer printing	Hardening with UV
Support structure requirements	Yes	No	Yes	No	Yes	Yes
Qualitative evaluation of AM parts						
Mechanical properties	+++-	++++	+	+	++	++

Table 1.1 Qualitative Evaluation of the AM Processes in Terms of Component Properties and
 Field of Applications