

Binding Mechanisms in Selective Laser Sintering and Selective Laser Melting

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Abstract

Layer Manufacturing (LM) technologies like Selective Laser Sintering (SLS) were developed in the late 80's as techniques for Rapid Prototyping (RP). Today, SLS - as well as its derived technology Selective Laser Melting (SLM) - is used as well for prototyping, tooling and manufacturing purposes. This widening of applications is caused mainly by the possibility to process a large variety of materials, resulting in a broad range of physical and mechanical properties.

This paper presents a survey of the various binding mechanisms in SLS and SLM, which are responsible for the broad range of materials and applications. Basic binding mechanisms involve solid state sintering, chemically induced binding, liquid phase sintering, partial melting and full melting. Many subcategories can be distinguished based on the type of structural or binder powder composition: single component powder grains (single material or alloy), composite powder grains, mixtures of different powder grains, distinct binder material (sacrificial or permanent), etc. The paper will explain how these binding mechanisms apply for sintering various types of materials: plastics, metal, ceramics and composites (e.g. glass reinforced polymers, cermets, hardmetals, etc.). It gives a survey of research done at the University of Leuven, Belgium, as well as at other European and non-European organizations.

Introduction

Selective Laser Sintering is a Layer Manufacturing process that allows generating complex 3D parts by consolidating successive layers of powder material on top of each other [1,2]. Consolidation is obtained by processing the selected areas using the thermal energy supplied by a focused laser beam. Using a beam deflection system (galvano mirrors), each layer is scanned according to its corresponding cross section as calculated from the CAD model. The deposition of successive powder layers with a typical thickness of 20 till 150 μm is realized using a powder deposition system.

Figure 1 shows a schematic example of an SLS system. Commercial machines differ for example in the way the powder is deposited (roller or scraper), the atmosphere (Ar or N₂) and in the type of laser they use (CO₂ laser, lamp or diode pumped Nd:YAG laser, disk or fiber laser).

Definitions and classification

Unlike Rapid Prototyping, Rapid Manufacturing and Rapid Tooling pursue the production of objects for long-term use. Rapid Manufacturing concerns the production of long-term consistent components (e.g. a dental implant) while Rapid Tooling concerns the production of long-term consistent tools (e.g. a plastic injection mould insert).

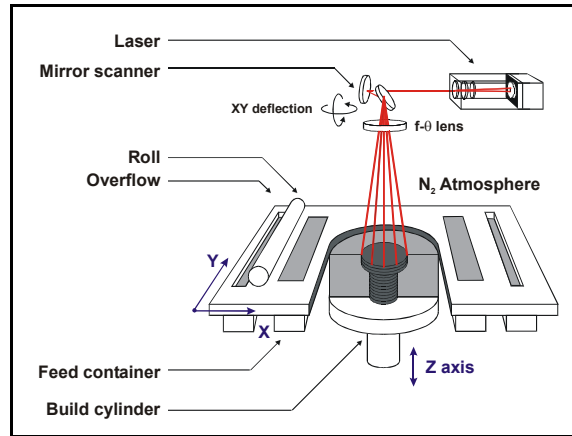


Figure 1 A typical SLS machine layout

RM and RT technologies can be classified in a number of ways [3]. Traditionally the technologies are being classified according to the materials they process (plastics, metals, ceramics or composites). In this survey, a classification according to the SLS binding mechanism is used.

Figure 2 shows a possible classification of SLS technologies according to the binding mechanism. Most SLS technologies can be classified using this type of classification, however some do not fit in only one section. For example SLS of glass reinforced polymers (e.g. Duraform™ GF being PA12 nylon material with 50 weight % glass) can be seen as Liquid Phase Sintering of composite powder grains regarding the polymer as a binder and the glass particles as a structural material. However, it can also be looked at as if it was a kind of ‘Full Melting’ of a single component composite powder, since the polymer does not just act as a binder material but constitutes the major phase of the structural material being glass filled polymer. Basically it is a structural material that is ‘fully’ molten, be it that its glass particles remain solid.

Next paragraph will shortly describe the different binding mechanisms and illustrate them with some examples of corresponding technologies.

Different binding mechanisms

This paragraph will discuss the state of the art in SLS and SLS-derived technologies. According to the binding mechanism, SLS technologies (and derived technologies like SLM and DMLS) can be classified in four categories. However it has to be noticed that this classification is not absolute and the borders are not always very clear.

1. Solid State Sintering (SSS)

Solid State Sintering is a thermal process that occurs at temperatures between $T_{Melt}/2$ and T_{Melt} , where T_{Melt} is the melting temperature of the material. Various physical and chemical reactions occur, the most important being diffusion [4]. It involves neck formation between adjacent powder particles (see Figure 3). The main driving force for sintering is the lowering of the free energy when particles grow together. A gradient in vacancy concentration between the highly curved neck (high vacancy concentration) and the ‘flat’ surfaces (low vacancy concentration) causes a flux of vacancies from the neck and a flux of atoms towards the neck thus increasing the neck size.

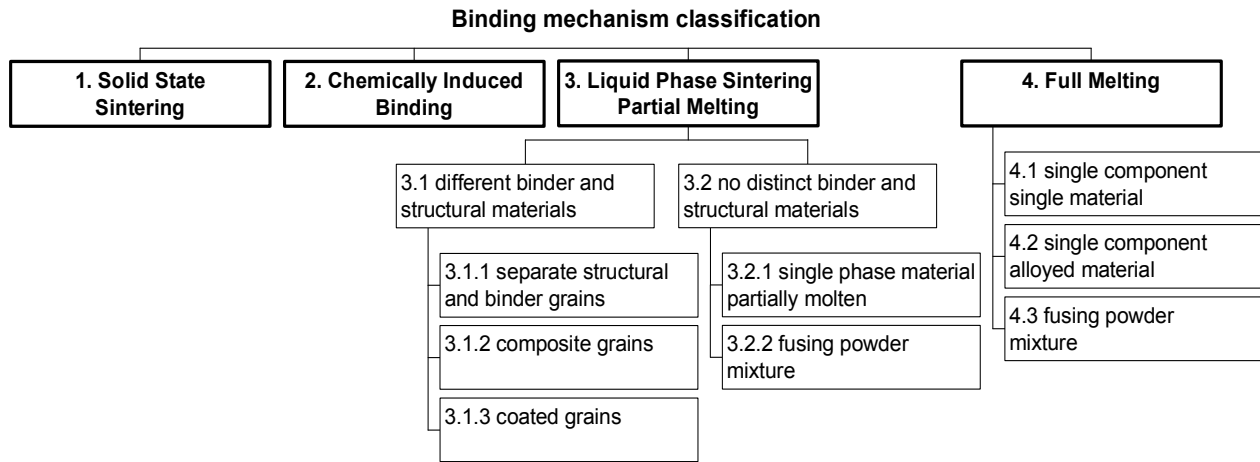


Figure 2 Classification of SLS-technologies according to binding mechanisms

The main advantage of Solid State Sintering is that a wide variety of materials can be processed this way. As long as the temperature is high enough to provide the necessary kinetic energy for the transport of vacancies across the grain boundaries, all powder materials will consolidate via volume diffusion [4]. However, it is a slow process and therefore preheating of the powder material is necessary to increase the diffusion rate of atoms and to obtain an acceptable laser scanning velocity.

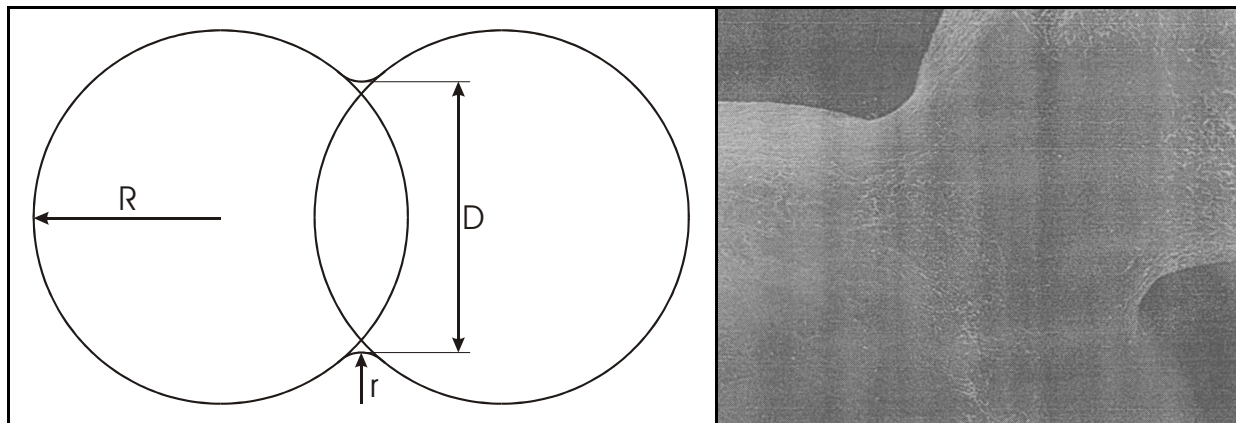


Figure 3 left: neck formation in Solid State Sintering [4], right: neck formation between two stainless steel powder particles

The National Academy of Science of Belarus, the Baikov Institute of Metallurgy (Russia) and the University of Leuven (Belgium) together investigated Solid State Sintering of titanium powder using ‘soft’ laser radiation [5]. The phenomenon was simulated using numerical models and the results were experimentally justified. To avoid problems related to Selective Laser Melting, titanium powder was consolidated using low intensity laser light ($100\text{-}300\text{ W/cm}^2$) for a long period of time (5 s). Since the temperature of the particles stayed well below the melting point of Ti, the only mechanism occurring was Solid State Sintering. The degree of sintering was quantified using the ratio of neck diameter to powder particle diameter ($D/2R$ in Figure 3). It was concluded that the degree of sintering was low as long as the temperature reached stayed below the α/β -transition temperature (890°C). Rising above this temperature, thus forming β -phase titanium resulted in a strong rise in sintering degree. This could be explained by the high self-diffusion coefficient of the β -phase compared to the α -phase.

Phenix Systems (France) commercializes an SLS-like system that realizes Solid State Sintering using a high temperature process chamber reaching up to 900 °C [6]. The compacted powder, which is close to the Solid State Sintering temperature, is sintered due to the energy contribution of a Nd:YAG laser source. This way, ceramic materials can be processed as well as metal powders. To obtain the desired characteristics, a post sintering operation is necessary. Figure 4 depicts some ceramic parts.

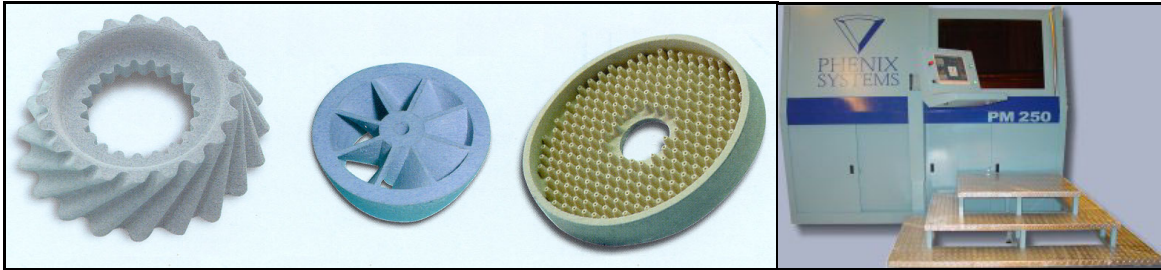


Figure 4 Solid state sintered ceramic parts (source: Phenix Systems)

2. Chemically Induced Binding

At the Fraunhofer Institute IPT (Aachen, Germany) the direct production of SiC ceramic parts has been investigated [7]. No binder elements were used and the laser-material interaction times were very short, thus excluding the diffusion processes occurring in Solid State Sintering. When heating the SiC particles to a very high temperature, partial disintegration of the SiC into Si and C occurs. The free Si forms SiO₂, which acts as a binder between the SiC particles. The parts are thus composed of a mixture of SiC and SiO₂. Afterwards an infiltration step using Si yields full dense parts.

Next to SiC, also other ceramics were tested, e.g. Al₂O₃ and ZrSiO₄. Figure 5 shows a ceramic casting shell produced by SLS.

An other example of chemical induced binding is the consolidation of Al powder in a N₂ atmosphere whereby an AlN binder phase is formed. This reaction is not yet used in Selective Laser processing, but Sercombe used it in an SLS post-curing process, after polymer debinding and before infiltration [15] (see paragraph 3.1.3 Coated grains).



Figure 5 SLS-produced investment casting shell for impeller wheel (source: Fraunhofer Institute IPT)

3. Liquid Phase Sintering (LPS) – Partial Melting

This category unites many different kinds of technologies. Most of these technologies combine a structural material remaining solid throughout the process and a binder material being liquefied. In some cases, however, the solid and the liquid phases result from the same material. A first group of technologies is characterized by a clear distinction between the binder and structural materials.

3.1 Different binder and structural materials

Technologies can be further divided into three groups according to the type of powder grains that is used.

3.1.1 Separate grains

These technologies use different binder and structural grains. The structural material can be a metal as well as a ceramic material; the binder materials however are mostly metals. Binder particles are usually much smaller than the structural ones. Therefore, the high surface-to-volume ratio of the grains – in combination with its relatively low melting point – favors the preferential melting of the binder material [8].

The combination of small binder particles and larger structural particles has the additional benefit of better packing with small pores favoring the spreading of the liquid binder by capillary forces and causes a rearrangement of the particles. Generally a ‘green’ part is produced which is still porous and brittle. Therefore, a post treatment consisting of a furnace post-sintering, Hot Isostatic Pressing (HIP) or an infiltration with a low melting point material is usually necessary. The last solution is most commonly used because of its effectiveness and its relative ease.

Figure 6 shows the LPS mechanism schematically. The solid line represents a conventional furnace sintering process. The LPS mechanism, as it occurs in SLS, is represented by the first part of the dashed line, since only the rearrangement phase takes place. The process is frozen at this stage resulting in a porous green product. A thermal post-treatment in a furnace may be used to complete the cycle.

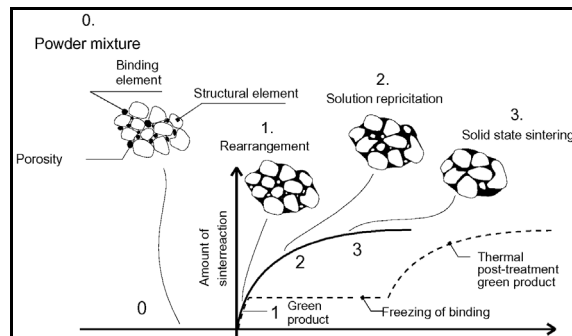


Figure 6 Mechanism of Liquid Phase Sintering

Many different material combinations have been tested in the past. At the University of Leuven, metal-metal composites were tested as well as metal-ceramic composites [9,10]. Some examples of metal-metal composites are Fe-Cu and Stainless Steel-Cu. As for the metal-ceramics combinations, WC-Cu, WC-Co, WC-CuFeCo, TiC-Ni/Co/Mo, ZrB₂-Cu and TiB₂-Ni were tested. Figure 7 and Figure 8 left show cross sections of a Stainless Steel-Cu and a WC-Co green part.

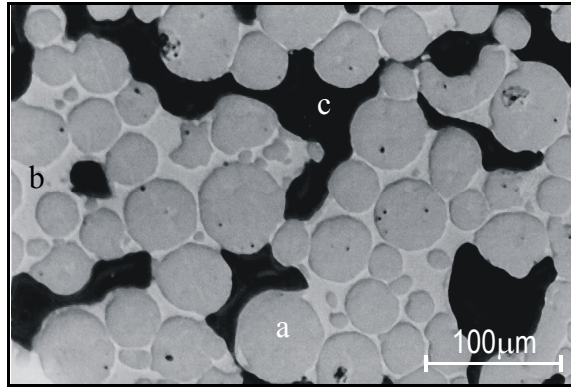


Figure 7 LPS of Stainless Steel-Cu powder mixture (a: non molten steel particle, b: molten Cu, c: porosity) (source: University of Leuven)

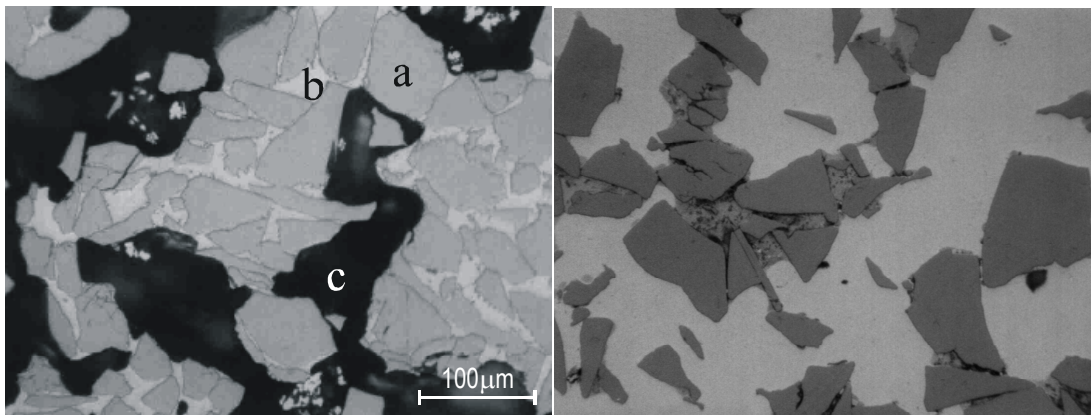


Figure 8 LPS of WC-Co powder mixture, left: before infiltration (a: non molten WC particle, b: molten Co, c: porosity), right: after infiltration with copper (source: University of Leuven)

3.1.2 Composite grains

Composite powder grains contain both the binder and the structural material within each individual powder grain. The powder may be obtained by mechanically alloying a mixture of two different powders, causing powder particles to be repeatedly milled, fractured and welded together.

Figure 9 a shows an initial powder mixture of WC and Co particles. Mechanical alloying results in WC-Co powder particles with a micro grain composite structure in which the two different phases (WC and Co) can still be identified (see Figure 9 b). Such composite grains result in a higher SLS green density and a better surface roughness than a mixture of separate WC and Co powders (see Figure 9) [10,11].

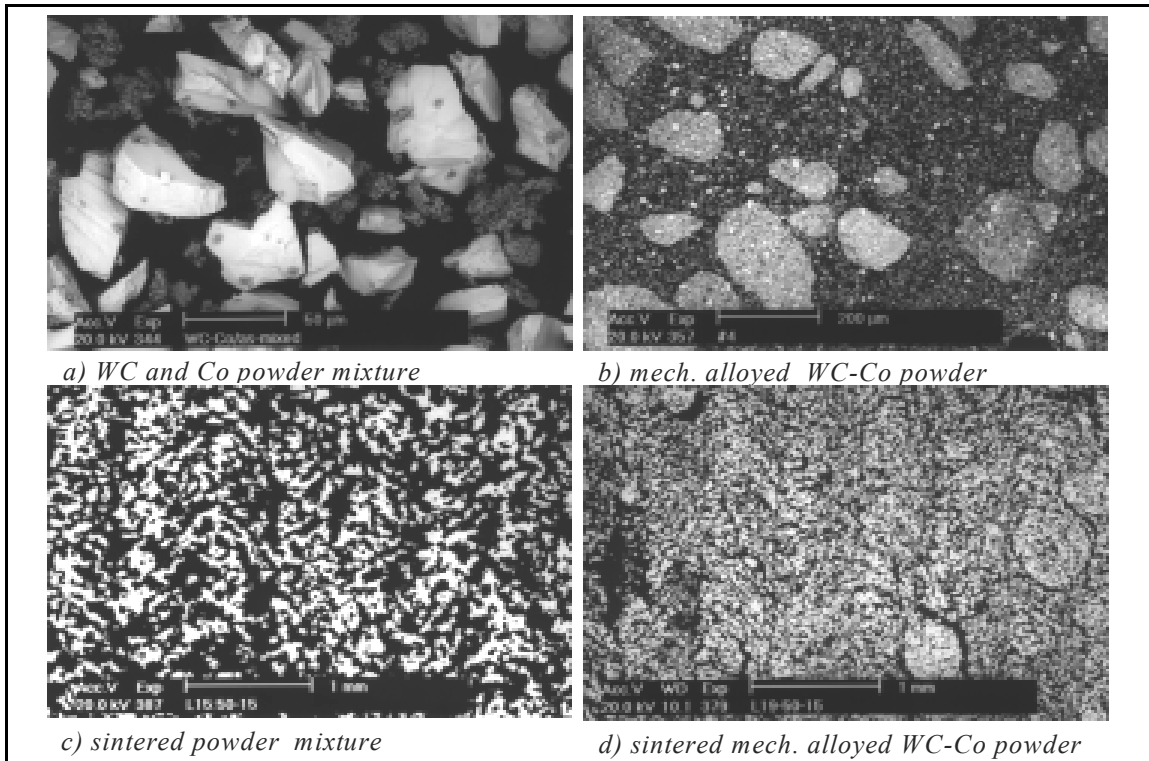


Figure 9 a) WC-Co powder mixture, b) mechanically alloyed WC-Co powder, c) sintered WC-Co powder mixture, d) sintered mechanically alloyed WC-Co powder (source: University of Leuven)

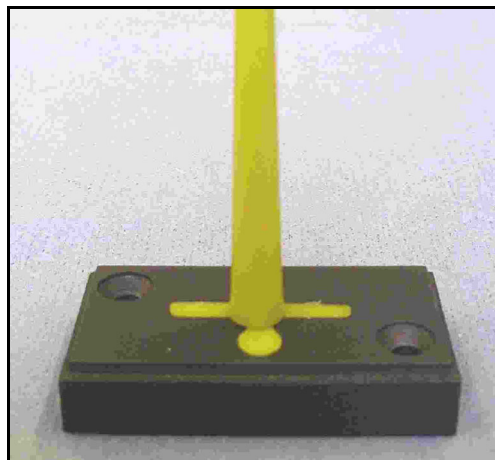


Figure 10 Bronze infiltrated WC-Co injection moulding insert (source: University of Leuven)

Figure 10 shows an example of a WC-Co injection-moulding insert.

Some polymer-based powders also consist of composite powder grains. An example is glass filled polymer powder [13]. Figure 11 left shows the microstructure of a sintered sample, indicating the spherical glass particles (some of which are removed from the nylon by grinding) and some zones of remaining porosity (filled with the sample's embedding material). The right side picture shows a low-weight, high-strength sandwich panel, which was made from the glass filled nylon material.

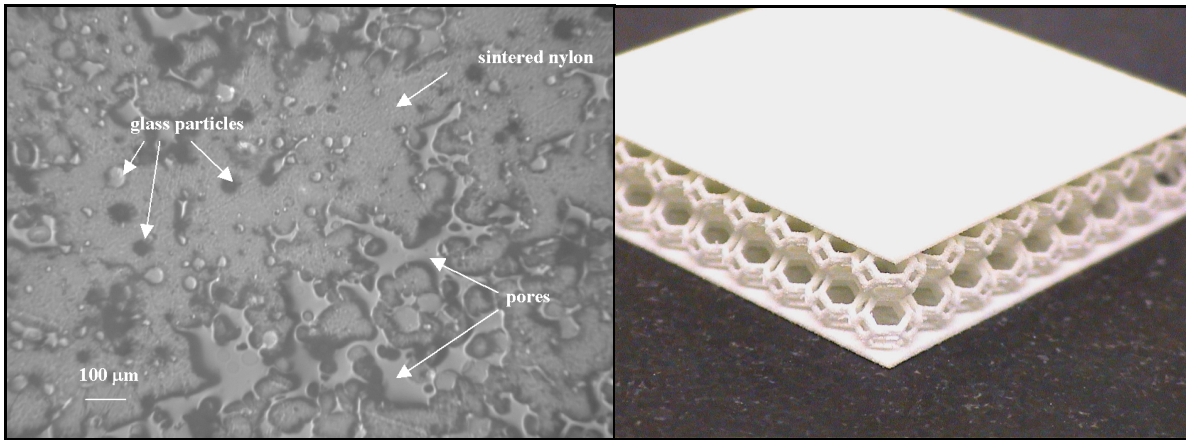


Figure 11 Left: cross section of a glass filled nylon part, right: light-weight sandwich panel made from glass filled nylon (source: University of Leuven)

3.1.3 Coated grains

A third possibility to combine a binder and a structural material is to coat the structural material with the binder phase. This ensures that the laser radiation hitting the powder particles is preferentially absorbed by the binder material that is to be melted: in the case of separate grains it may happen that the structural material (e.g. Fe) absorbs more laser energy than the binder material (e.g. Cu) causing the structural material to melt before the binder does [12]. Moreover a more effective bonding of the structural particles is realized since the binder material already surrounds all structural particles. Coated powders exist both with metal and polymer binder coatings.

At the University of Leuven, experiments with Cu coated steel powder turned out to be successful despite of the fact that the powder coating process was hard to control [4].

Polymer coated steel powders (DirectSteel and LaserForm) are commercially produced by 3D Systems [13], formerly DTM Corporation. Most polymer coated powders need an additional debinding step in which the polymer is burnt out. Afterwards an infiltration step is possible. Figure 12 shows a cross section of an SLS part made from polymer coated stainless steel powder (LaserForm), after polymer debinding and infiltration with bronze.

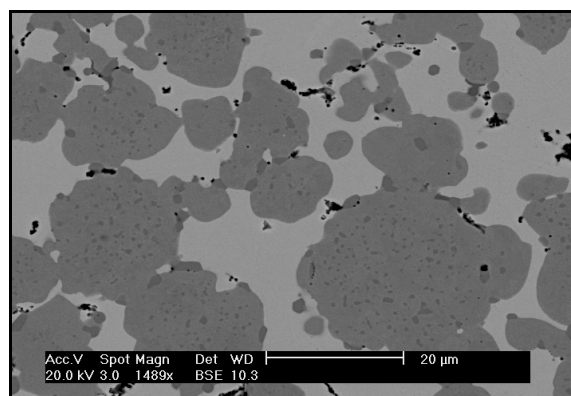


Figure 12 Bronze infiltrated Laserform ST 100 part

However, polymer coated powders may also be applied without debinding in order to produce e.g. polymer/metal composite parts. An example of this is polyamide coated copper

powder used on DTM machines to produce copper reinforced polyamide moulds for injection moulding [14].

At the University of Queensland, an aluminium sintering process was developed in collaborations with 3D Systems [15, 16]. Since the strong oxide layer on the grains prohibits direct sintering of Al powder, an indirect procedure was developed. Nylon coated Al grains are fused together using the LPS mechanism. Next, the nylon binder is decomposed. A small amount of magnesium added to the powder mixture makes it possible to form aluminium nitride instead of aluminium oxide when heating up to 540 °C. The aluminium nitride acts as a rigid skeleton, which is necessary during the infiltration phase. The infiltrant being used is a ternary eutectic aluminium alloy (Al-13.8Si-4.7Mg), having a lower melting point than the basic aluminum alloy. Relative part densities up to 95 % were obtained. Figure 13 shows the different processing steps.

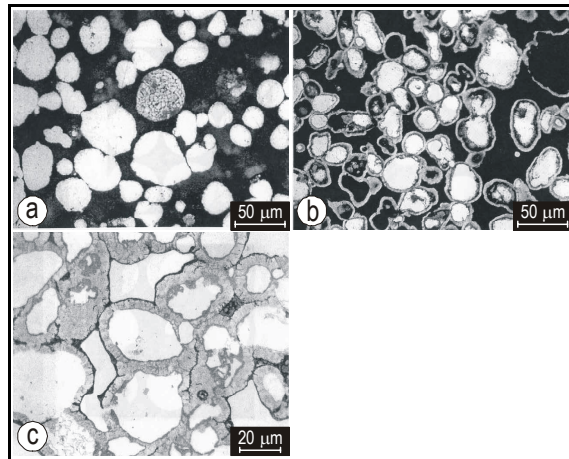


Figure 13 Steps in Aluminium SLS: a) green part (nylon binder not visible) b) aluminium nitride skeleton surrounding the aluminium grains, c) infiltrated part

A last type of coated powders are the sand powders developed DTM- 3D Systems (SandForm) as well as by EOS GmbH (Direct Cronging) [17]. The powders offered are standard Si of Zr sands, coated with a small phenolic layer, responsible for fusing the sand grains together. These powders are used to produce moulds and cores for metal casting.

3.2 No distinct binder and structural material

Technologies in this group do not exhibit a clear distinction between binder and structural phases. Rather than the distinction between binder and structural material, there is a distinction between molten and non-molten material areas. Therefore ‘Partial Melting’ is a better name for these technologies than ‘Liquid Phase Sintering’.

3.2.1 Single phase, partially molten

When the heat supplied to a powder particle is insufficient to melt the whole particle, only a shell at the grain border is molten. The core of the grain stays unaffected. This way the molten material acts as a binder between the non-molten particle cores. This binding mechanism can arise as well with metals as with polymers, although the consolidation of polymer powders results also from other mechanisms (consolidation at the glass transition temperature, which is lower than the melting temperature, polymer chain rearrangement and cross-linking).

The partial melting phenomenon was modeled by Karapatis [8]. Using a simple thermal model, skin and core temperatures of the powder particles were calculated. This way the minimal

pulse energy to fully melt the particle can be calculated. Below this value, the core temperature never exceeds the melting temperature and only partial melting is obtained.

3.2.2 Fusing powder mixture

Powders consisting of multiple phases can be classified in this group when they are only partially molten. For example at the University of Leuven experiments were done with a Fe-Fe₃P-Ni-Cu powder mixture, aiming at the production of full density parts [18]. The addition of a melting point lowering additive like Fe₃P is favourable in making the process more energy efficient. For instance, alloying pure Fe with a small amount of P lowers the melting point of pure Fe (1538°C) to the eutectic temperature of the Fe-P system (1048°C, see Figure 14). Moreover, the dissolution of P in Fe also has the benefit of a lower surface tension of the melt, resulting in a better wetting behaviour. Ni is added for its marked strengthening effect.

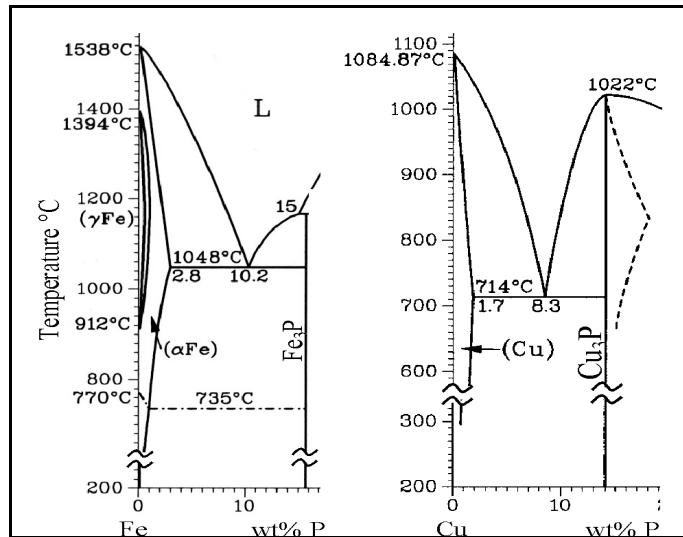


Figure 14 Phase diagrams of Fe-P and Cu-P showing the temperature lowering effect of the added P

A closer look at the microstructure reveals that not all the powder particles are molten (see Figure 15). The final part consists of a low melting point P-rich phase (no. 3), a high melting point phase with no significant amount of P (no. 2), some remaining porosities (no. 4) and some remaining unmolten Fe powder particles (no. 1). Therefore, the process cannot be called ‘full melting’ and the name ‘partial melting’ is preferred.

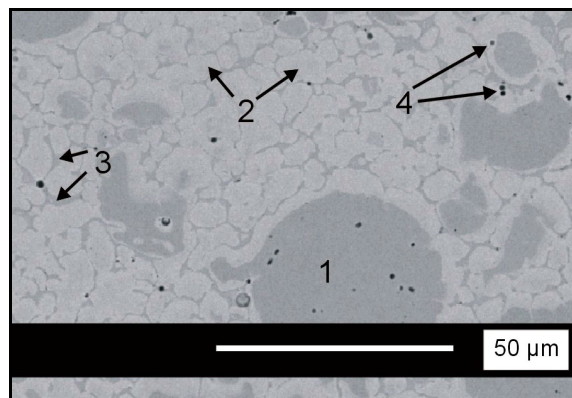


Figure 15 Micrograph of multiphase steel powder: 1) unmolten Fe particle, 2) high melting P-poor phase, 3) low melting P-rich phase, 4) pores (source: University of Leuven)

EOS' Direct Metal Laser Sintering process also belongs to this category [17]. The recent introduction of 20 μm metal powders brings an improvement in mechanical properties and surface quality. Figure 16 and Figure 17 show the difference in porosity between a 50 μm and a 20 μm powder. In both cases shot peening enhances surface quality and improves the density of the top layer. Different parameter sets are used for the part's skin and core, in order to obtain a rigid and hard shell and at the same time a higher building speed (by fast scanning of the core).

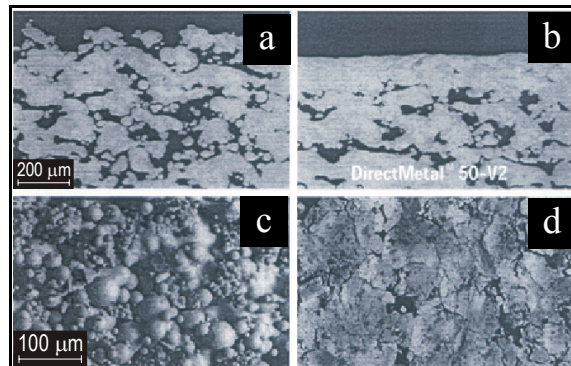


Figure 16 DMLS Direct-Metal 50V-2 grain size 50 μm , porosity 10-15%: a and c before shot-peening, b and d after shot peening (a and b: cross section, c and d: top view)(Source EOS)

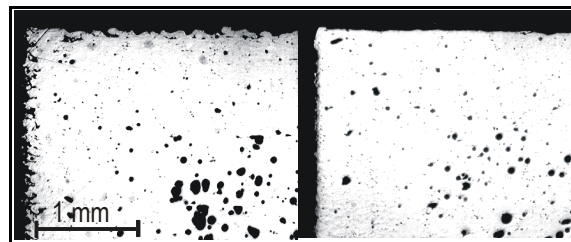


Figure 17 DMLS Direct-Steel 20V-2 grain size 20 μm , porosity ~ 5%, in the ZX plane: left before and right after shot-peening, cross section (Source IPT)

Table 1 concludes the third bonding category by summarizing some important mechanical properties of commercially available materials.

	Reference		SLS materials										
	Reference Steel: P20	Reference Al 7075 Zn Mg Cu 0.5	DTM RapidSteel 1.0	DTM RapidSteel 2.0	3D Systems LaserForm ST 100 (St. Steel)	3D Systems LaserForm ST 200 (St. Steel)	3D Systems LaserForm A6	EOS Ni - Bronze (Electrolux)	EOS DirectMetal™ 100 – V3 (Bronze)	EOS DirectMetal™ 50 – V2 (Bronze)	EOS Directsteel™ 50 – V1	EOS DirectMetal™ 20 – V2 (Bronze)	EOS Directsteel™ 20 – V1
Grain size [μm]	-	-	50	45	23 ¹	20 ¹	-	100	100	50	50	20	20
Infiltrant ²	-	-	C	B	B	B	B	E	-	-	-	-	-
Tensile Strength MPa	950	570	475	580	510	435	610	162	199	199	499	450	600
Yield Strength 0.20%	751	502	255	413	305	n.a	470	124	n.a	n.a	n.a	n.a	n.a
Young's Modulus GPa	210	65	210	263	137	142	138	60	n.a	50	110	80	130

Table 1 - Commercial SLS metal powder systems and their mechanical properties (¹ d₅₀, ² C = Copper, B = Bronze, E = epoxy resin)

4. Full Melting

Driven by the need to produce near full dense objects, with mechanical properties comparable to those of bulk materials and by the desire to avoid lengthy post processing cycles, Selective Laser Melting has been developed. Polymers as well as metals can be completely molten by a laser beam. However, the appellation Selective Laser Melting (SLM) is reserved for metallic materials. Therefore, polymers will not be discussed in this section.

All metals may be thought as candidate material however large differences exist in the ease of processing (e.g. laser absorption, surface tension and viscosity of the liquid metal, etc.). For each new material, a process-window needs to be determined experimentally, in order to avoid scan track instabilities (sphereodisation of the liquid melt pool, also known as ‘balling’) and part porosity. Therefore the range of commercially available SLM metals is still limited today. Figure 18 shows an example of such a process window for an iron based powder mixture.

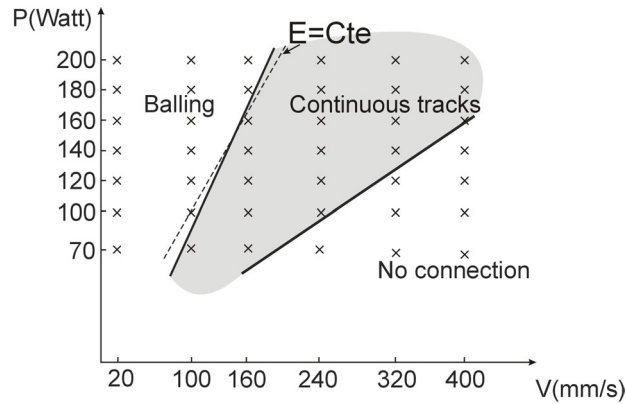


Figure 18 SLM process window for an iron based powder mixture (source: University of Leuven)

4.1 Single component, single material powder

The Fraunhofer Institute ILT [19] as well as the Universities of Osaka [20] and Leuven, performed a lot of investigation on Selective Laser Melting of pure titanium powder. Figure 19 shows a titanium part that was produced with SLM. It can be seen that the part density is almost 100%, however the picture also reveals a crack (bottom left) caused by thermal stress, which needs to be reduced in the future. It is expected that commercial titanium SLM will be offered soon.

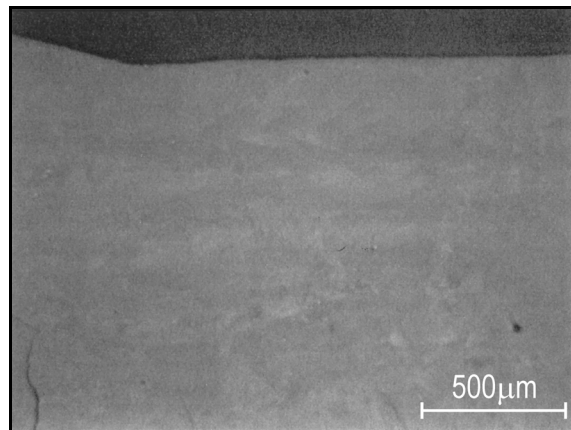


Figure 19 Cross section of a Ti part produced by Selective Laser Melting (source: University of Leuven)

4.2 Single component, alloyed powder particles

These powders consist of a single kind of grains, consisting of alloyed materials. Many different kinds of alloys have been tested and some are already commercially available through the three German manufacturers of SLM machines (Concept Laser GmbH [21], Trumpf [22] and MCP-HEK [23]). The Fraunhofer Institute ILT for example has investigated Stainless Steel 1.4404 and Tool Steel 1.2343 [24]. Figure 20 shows an example of a stainless steel part.

Next to the steel powders, also a titanium alloy (TiAl6V4) was tested for the manufacturing of medical implants.

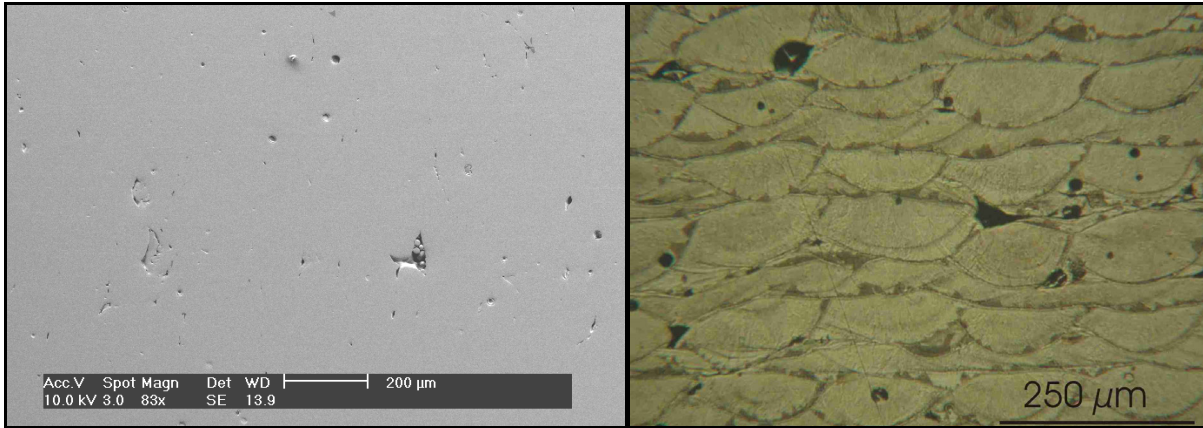


Figure 20 Cross section of a stainless steel 1.4404 part produced by Selective Laser Melting (source: Trumpf)

Figure 21 compares the mechanical properties of parts made of steel 1.4404 with those of the bulk material. It can be concluded that mechanical properties are comparable to bulk material apart from the ductility, which is strongly reduced. This might be overcome applying the right heat treatment. More detailed data are presented in table 2.

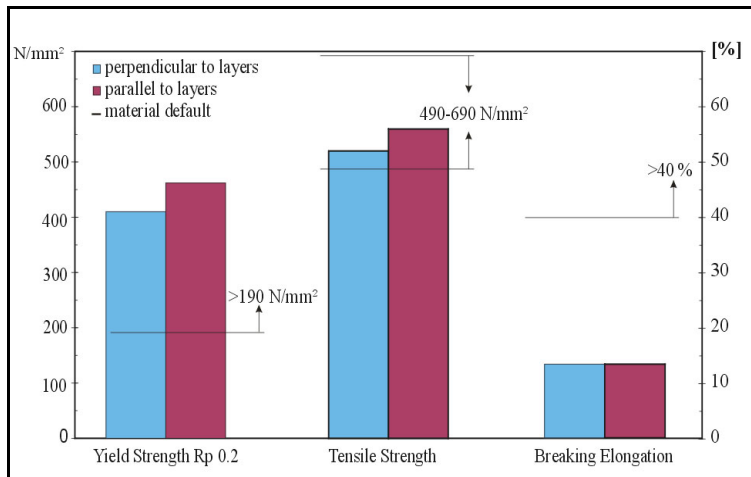


Figure 21 Comparison SLM part properties and standard bulk material properties for stainless steel 1.4404 (Source ILT)

Material	Stainless Steel 1.4404	Tool Steel 1.2343	TiAl6V4
Tensile Strength (MPa)	480-520	780-840	1200-1400
Elongation (%)	10-15	2-3	1-2
Hardness	220-250 HV0.1	50-54 Rockwell	380-420 HV0.3
Surface finish (μm)	R _z 30-60	R _z 30-60	R _z 30-60
Accuracy (mm)	± 0.1	± 0.1	± 0.1
Density (%)	ca. 100%	ca. 100%	ca. 100%

Table 2 - Mechanical properties of available SLM metals

4.3 Fusing powder mixture

Depending on the degree of melting one can classify some processes using powder mixtures under Selective Laser Melting (all powder particles melt) or Partial Melting (some powder particles remain non molten). The powders and sintered parts depicted in Figure 15 illustrate that the border between ‘partial melting’ and ‘full melting’ is rather vague, at least when near-full density parts are aimed for.

Conclusions

Over the last decade Rapid Prototyping techniques gained a wide acceptance. Among the different RP techniques, Selective Laser Sintering had the advantage of being able to process a wide range of materials. This large variety of materials gradually allowed to extend the field of applications, from simple visual prototyping to functional prototyping, and even Rapid Tooling and Rapid Manufacturing applications.

In recent years, the idea of full melting metal powders was explored, supported by the continuously improving process parameters (smaller layer thickness, smaller spot size, etc.), resulting in mechanical properties being much better than those of early time selective laser sintered parts and comparable with bulk metal properties. Rapid Tooling and specially Rapid Manufacturing technologies are still limited in use, but they are steadily growing. It can be expected that in the next decade they will achieve the same level of acceptance as Rapid Prototyping, by continuous improvement of material properties and accuracy and by a decrease of the costs.

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