New Ferro Powder for Selective Laser Sintering of Dense Parts

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Abstract

The paper describes a new powder composition specially developed for selective laser sintering (SLS). The aim is to obtain a ferro powder that can be sintered without need for a (sacrificial) polymer binder and that results in quasi dense parts that do not need any post-processing like furnace sintering, infiltration or HIP. The powder is a mixture of different types of particles (Fe, Cu, Ni and Fe₃P). The composition and mixture ratio are justified by using phase diagrams. The powder has been tested using an own developed Nd:YAG SLS machine. The influence of process parameters (laser power, scan velocity, scan spacing and scan strategy) and the microstructural characteristics have been investigated. Attention is devoted to the binding mechanism (liquid phase sintering, through melting) and to the quality of resulting parts (density, balling effect, ...).

Keywords:

laser sintering, iron powder, rapid prototyping

1 INTRODUCTION

For the production of functional metallic prototypes, parts or tools, a high density is desired. This can be obtained through different powder binding mechanisms [1, 2]. So far, liquid phase sintering SLS processes [3, 4] only allowed the achievement of 'green' densities up to 70%: full density could only be obtained by applying a secondary furnace infiltration step, which is very time consuming. The same holds for SLS processes that apply a sacrificial polymer binder which needs to be debinded in a furnace before further metal infiltration [5]. In order to reach near full density without furnace post-processing, techniques have been developed in which the metallic powder particles are fully molten. They are known as Direct Metal Laser Sintering (DMLS) [6, 7] or Selective Laser Melting (SLM) [8]. In this study new powder mixtures are developed having a similar composition as DirectSteel 50V1 powder [6,9] aiming at a high density and good mechanical properties.

Unlike liquid phase SLS processes (LP-SLS), selective laser melting (M-SLS) is more difficult to control. To minimise problems like 'balling' and deformation, the different process parameters have to be adjusted very well. Therefore a large amount of tests had to be done to define a narrow process window.

2 POWDER PROPERTIES

In choosing an appropriate powder mixture some considerations are taken into account (Table 1). The addition of a melting point lowering additive, e.g. Fe₃P or Cu₃P (Figure 1) is favourable in making the process more energy efficient. For instance, pure Fe has a melting point of 1538°C and after alloying with a small amount of P this can be lowered to 1048°C (Figure 1a). The dissolution of P in Fe also has the benefit of lowering the surface tension of the melt [11]. This lowers the tendency to form balls after melting and thus enhances the surface quality. Another advantageous property of P is lowering of the oxidation rate of the Cu and Fe powder particles. A last effect is an increase in hardness. Ni is added for its marked strengthening effect although its toxicity makes it an unpopular material. Attention is also paid to the compatibility of the different elements: they form intermetallic phases like (Fe,Ni)₃P. The effect of the powder shape is tested by using mixtures with either spherical or irregular structural Fe particles. All the other powder particles are spherical.

The irregular powder has an apparent density of 3.17 g/cm³ and a true density of 8.01 g/cm³ while the spherical powder has a higher apparent density, 3.75 g/cm³, due to the improved packing of spherical particles [12].

	Irregular Fe < 60 µm	spherical Fe < 50 µm	spherical Ni 5 µm	spherical Cu < 50 µm	spherical Fe ₃ P < 50 µm
Powder 1	50 %		20 %	15 %	15 %
Powder 2		50 %	20 %	15 %	15 %

Table 1: Composition of the powder mixtures (weight %).

Figure 1: Phase diagram of (a) Fe-P and (b) Cu-P at small weight % of P [10].

3 EXPERIMENTAL CONDITIONS

The machine used to perform the experiments was built at the University of Leuven. It uses a Rofin-Sinar Nd:Yag laser source with a wavelength of 1.064 μm and a maximum output power of 300 W in continuous mode. Operation in pulsed mode with a frequency between 0 and 500 Hz is also possible. Using galvano-mirrors, the scan speed can be as high as 5000 mm/s. By means of a stepper motor the build platform can be moved with a resolution of 10 μm . Powder layers are deposited in one direction using a roller. The building stage is put in a vacuum chamber that can be filled with nitrogen or argon to prevent oxidation of the parts. The high shrinkage forces during M-SLS solidification necessitate the use of a base plate, which is bolted to the piston and to which the first sintered powder layers will be anchored through SLS to avoid part deformation (warping).

In this study the laser power is used at its maximum level (100 W for a 3 mm diaphragm) in order to speed up the process and the quality of the part. Variations in energy density (Equation 1) can be obtained by changing the scan speed or the scan spacing. Values of E_{density} between 4 and 6 J/mm² are used.

$$E_{\text{density}} = \frac{P_{\text{laser}}}{v_{\text{scan}} \cdot d_{\text{scanspacing}}} \left[\frac{\text{J}}{\text{mm}^2} \right] \quad (1)$$

The influence of initial temperature on the quality is investigated by comparing the layers after scanning with and without preheating. Preheating is appealing when it comes to lowering the required energy density and therefore to raising the scanning speed. The preheating is done by scanning the part with the laser out of focus by moving the part piston down. The attained temperature is more or less 500°C.

4 RESULTS AND DISCUSSION

4.1 Microstructure characteristics

Investigation of the microstructure has been performed by a Philips SEM XL 30 FEG scanning electron

microscope. The best results with the powder containing irregular Fe particles and with the laser operating in continuous mode are obtained at a scan speed of 200 mm/s, a power of 100 W, a scan spacing of 0.1 mm and a layer thickness of 150 μm (Figure 2a). This gives a value of 5 J/mm² for E_{density} (Equation 1). A test is also performed by scanning in pulsed mode (Figure 2b). The latter leads to a relative density of 86% while in continuous mode the density is only 72%. However working in pulsed mode has the disadvantage of a much lower process speed. For the spherical powder the same conditions in continuous mode are used but the layer thickness could be reduced to 80 μm (Figure 2c). It can be seen on Figure 2 that this reduction in layer thickness has a beneficial effect on the density, which is now 76%.

To understand the mechanism occurring during laser processing a closer look is taken at the micrographs (Figure 3). The final part consists of a low melting point P-rich phase, a high melting phase with no significant amount of P present and some remaining Fe powder particles. The percentage of Cu and Ni is almost equally divided between the former 2 phases. This requires a rapid diffusion which is only possible when there is a high quantity of liquid phase. So it can be concluded that the process is rather laser melting than sintering.

Figure 2: Cross-sectional micrograph of a part built using irregular Fe powder in (a) continuous and (b) pulsed mode; (c) using spherical Fe particles in continuous mode. Notice that the magnification is a lot smaller than in Figure 3.

Figure 3: Micrograph after laser sintering of powder 2 showing some remaining Fe particles (1), the dendritic P-poor high-melting phase (2) surrounded by the darker inter-granular P-rich divorced eutectic (3) and some residual porosity visual as black dots (4).

A differential scanning calorimeter (DSC) scan with a heating and cooling rate of 10°C/min and a maximum temperature of 1400°C is performed in order to study the behaviour during cooling and solidification. This rate is however not comparable with SLS rates (some 10°C per millisecond during cooling) but gives a first idea of the temperature at which phase transitions are occurring. During cooling a first phase begins to solidify at 1370°C over a broad temperature range. In order to understand the microstructural evolution, one can use the Fe-Ni-P ternary phase diagram as a first approximation [13]. On this diagram it can be seen that this first solidifying phase corresponds to the γ phase containing Fe, Ni and some P. This phase solidifies under the form of dendrites (Figure 3). The amount of P in the γ -phase diminishes during further cooling until in a narrow region around 910°C the remaining liquid solidifies. At that temperature the %P in the liquid corresponds to a binary eutectic composition [13]. This eutectic contains the γ and (Fe, Ni)₃P phase in the ideal case. From Figure 3 it can be seen that the low melting phase does not consists of two separate phases but only of one phase. An Energy Dispersive X-ray analysis shows that this phase is the (Fe, Ni)₃P phase. So the eutectic is divorced. This is probably due to the low surface tension of the (Fe, Ni)₃P phase promoting the coalescence of the eutectic γ phase and the dendritic γ phase.

The presence of a high quantity of liquid has the advantage that the pores of the previously sintered layers can be filled by action of gravity and capillary forces. From Figure 2a it can be concluded that a layer thickness of 150 μ m is too high for the melt to be able to fully penetrate all the pores. A disadvantage of a high quantity of liquid is the high sensitivity of the resulting part to the process parameters. This is due to the surface tension which tends to spheroidise the liquid resulting in a bad surface quality (Figure 4). This causes the powder deposition system to jam during deposition of subsequent layers, poor interlayer bonding and a higher porosity.

Consider a flat, undeformable, perfectly smooth and chemically homogeneous solid surface (S) in contact with a non-reactive liquid (L) in the presence of a vapour (V) phase (Figure 5). If the liquid does not completely cover the solid, the liquid surface will intersect the solid surface at a contact angle θ that corresponds to a minimum of the total free energy of the system. The value of θ obeys the classical equation of Young (1804) (Figure 5). During the first rapid stage a metastable equilibrium is set followed by a much slower process (order of a minute) occurring at the vicinity of the triple line to satisfy the requirements of a stable local equilibrium given by Smith (1948). Since the interaction time during laser sintering is very short, order of magnitude of milliseconds, the equation of Young holds.

Figure 4: Surface of a laser sintered part showing the balling effect.

Figure 5: The wetting of a liquid on a solid substrate with σ_{SV} , σ_{SL} and σ_{LV} the surface free energies of the system [14].

To improve the wetting behaviour the wetting angle θ should be as small as possible, so the value of σ_{LV} should be small in comparison with the difference between σ_{SV} and σ_{SL} . The former value is dependent on the temperature and for liquid Fe this can be expressed as (T_m denoting the melting temperature) [14]:

$$\sigma_{LV}^{Fe}(T) = 1855 - 0.23(T - T_m) \text{ [mJ/m}^2\text{]} \quad (2)$$

Equation 2 shows that σ_{LV} diminishes, so the wetting enhances, with increasing temperature. This explains the beneficial effect of preheating, and the resultant higher obtained temperature, on wetting. On Figure 6 the higher layer density due to a better spreading of the melt when applying preheating is visual.

Another possibility to improve the wetting is adding certain specific alloying elements, like P in this study [14].

Working in a reducing atmosphere leads to a lower contact angle than an inert or high vacuum atmosphere if the substrate has adsorbed oxygen [14]. It is also very important to avoid oxidation of the substrate since liquid metals do not wet surface oxide films in the absence of a chemical reaction [15].

The spheroidisation is also dependent on the ratio of the length to the width of the melt track, which is in turn dependent on the process parameters. As shown in Figure 7, to prevent balling the melt length relatively to the width should be kept as small as possible [12]. This requires that the melt pool resolidifies rapidly behind the laser spot (short melt length).

Next to balling, thermal deformation is another problem encountered during M-SLS. Preheating is in this respect also beneficial since it reduces the temperature gradients. Without preheating, the contraction of the upper layer due to its cooling, causes the part to bend, as shown in Figure 8. Preheating has also the benefit of increasing the energy incoupling due to the increased absorptivity of metal powder with raising temperature [12].

Figure 6: Cross-section of a single layer sintered without (a) and with (b) preheating using powder consisting of irregular Fe particles.

Figure 7: The dependence of balling on the dimensions of the molten laser track.

Figure 8: Thermal deformation of a part after laser sintering.

The problem of deformation is however not solved by only eliminating thermal gradients. There is also a volume change, either swelling or shrinkage during solidification. In the present study this deformation is minimised by mixing appropriate materials together. These form intermetallic phases during solidification, which compensate the shrinkage due to rearrangement of the particles. Since it was not possible to fully eliminate the high bending deformation, parts had to be produced on a base plate.

4.2 Mechanical properties

The properties of parts made using irregular Fe particles are identified. Three point bending tests are done (according to the ASTM B312-82 standard) on parts using powder 1 (Table 1) to investigate the strength of the material. All the tests on parts made at different process parameters in continuous laser mode reveal bad inter-layer connections. When applying a load along the layer orientation, a strength of 380 MPa is obtained. Rotating the part 90°C and applying the load perpendicular to the layer orientation, leads to a strength of 290 MPa, due to layer delamination. In pulsed mode a strength of 395 MPa is obtained perpendicular to the layer direction. This is confirmed by the micrographs showing a much better inter-layer connection in the latter case (Figure 3). The average micro-Vickers hardness (load 25 g) is 220 and the Rockwell B hardness is 45 for the parts made in pulsed and continuous laser mode. The elastic modulus E is measured with a Grindosonic. A value of 67 GPa was obtained. The surface roughness was determined on a sample without any post-treatment. A R_a value of 17 μm was measured, using a cut-off wavelength of 2.5 mm.

5 CONCLUSIONS

This paper has demonstrated the importance of the powder composition, powder morphology and processing parameters in striving to obtain fully dense metal parts by selective laser melting of metal powders. SEM micrographs were used to analyse the metallographic structure and porosity of the resulting parts.

It is shown that spherical particles, working under pulsed laser mode and preheating are factors promoting a high density.

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7 REFERENCES

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