On Some Physical Aspects of Process Control in Direct Selective Laser Sintering of Metals—Part I

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1 Introduction

Selective laser sintering (SLS) of metals is a complex process exhibiting multiple modes of heat, mass and momentum transfer, and chemical reactions. The strong interplay between these physical mechanisms directly impacts the SLS process, determining whether a given material can be processed and if so, how the microstructure and properties of the processed material are influenced. In order to understand the complex nature of these mechanisms, their interplay and impact on process control in SLS, it is appropriate to first understand them at a fundamental level. The next step should involve developing simple models that can quantitatively reveal the influence of these mechanisms as functions of processing conditions. Following this step, increasingly detailed models that take into account the coupling between different mechanisms should be developed.

In this review paper, a first step is taken towards identifying and understanding some of the important physical mechanisms in direct SLS. This study not only provides an insight into phenomena observed during direct SLS of a variety of metallic materials, but also helps in selecting materials that are most amenable to processing by direct SLS. Physical mechanisms discussed include oxidation, wetting, epitaxial solidification, elemental vaporization, melt flow instabilities and powder bed caking. Understanding these physical mechanisms is essential for the design of direct SLS machines and their process control.

2 Wetting

2.1 Effect of Processing Atmosphere on Wettability

Direct SLS of metals is far more demanding than SLS of polymers or indirect SLS of metals. Oxidation is a serious problem at the higher processing temperatures necessary for melting metals of interest (typically exceeding $> 1000°$C). Since selective laser sintering is a layerwise additive process, oxidation of laser processed powder is a severe impediment to interlayer bonding and causes defects such as balling. Balling occurs when the molten metal does not wet the underlying substrate due to an oxide layer being present on the substrate and on the surface of the melt. Oxidation also causes delamination induced by poor interlayer bonding in combination with thermal stresses. These phenomena severely degrade material properties and part geometry.

Poor wetting of an oxide substrate by a liquid metal is explained by the interfacial thermodynamics involved. The equilibrium of a liquid in contact with non-interacting solid and gaseous phases is shown in Figure 1. The equilibrium of interfacial free energies γ_{ij} is governed by

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \tag{1}$$

The liquid will wet the substrate as $\cos\theta \to 1$ or equivalently, if $\gamma_{LV} < \gamma_{SV} - \gamma_{SL}$. This corresponds to the case on the left. The difference $\gamma_{SV} - \gamma_{SL} - \gamma_{LV}$ is termed the spreading coefficient S. Large, positive S favors spreading. Surface free energies of metal oxides are much lower than the corresponding liquid-vapor surface free energy. Thus, in the absence of a chemical reaction between the liquid and the substrate, liquid metals do not wet surface oxide films, preferring to minimize surface area by balling instead.

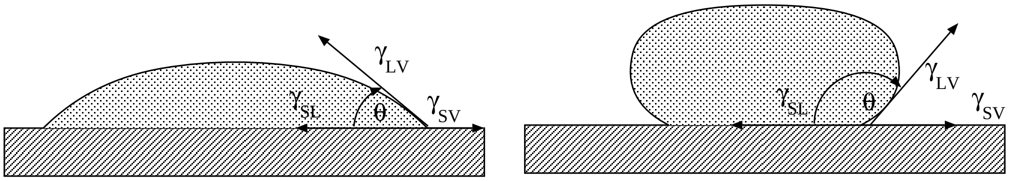

Figure 1: Three phase equilibrium for wetting and non-wetting systems.

To ensure good wetting and successful layer-by-layer consolidation direct SLS of metals, processing must be conducted in a vacuum or protective atmosphere using high purity inert gases. An Ellingham diagram [1] of common oxides shows that at the melting points of Nickel (1454.4°C), Chromium (1857°C) and Titanium (1704.4°C), the equilibrium partial pressure of oxygen must be less than 10^{-5}, 10^{-12} and 10^{-16} atm. respectively to prevent the oxidation reaction. Therefore, some oxidation cannot be avoided under normal operating conditions. In traditional furnace brazing operations for metals and alloys conducted under pure hydrogen atmosphere, it is important to consider the dew point or moisture content of the atmosphere against the most stable oxide forming element. A chart of metal-metal oxide equilibria under pure hydrogen at 1 atm is available in the literature [2]. This chart, calculated for a variety of metal oxides shows the temperature and water

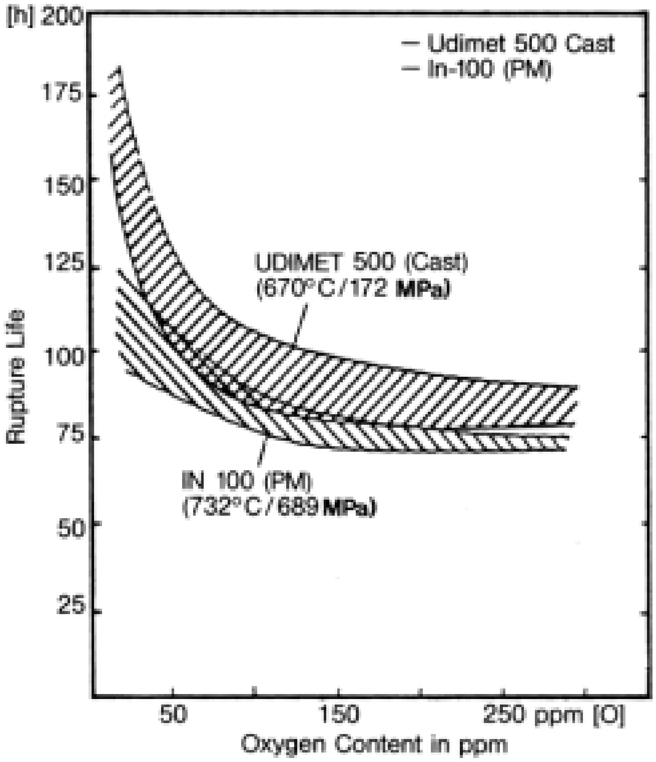

Figure 2: Influence of Oxygen on rupture life, after Choudhry (1990)

vapor partial pressure combinations under which the reaction is reducing or oxidising. For good wetting to take place, reduction of surface oxides is necessary to provide a clean metal-metal interface. Conventional practice involves providing a continuous flow of hydrogen to maintain the water vapor partial pressure levels favorably. It has been noted that the same chart is equally applicable for continuous flow inert gas atmospheres with similar oxygen content.

Some extremely reactive metals such as titanium cannot be processed under hydrogen atmospheres for two reasons. First, it is difficult to obtain hydrogen of the necessary purity at the processing temperature of interest (*i.e.* the melt temperature) . Second, titanium and its alloys are extremely sensitive to hydrogen embrittlement. Thus, traditional high temperature sintering and vacuum brazing is conducted in the 10^{-4}–10^{-6} Torr vacuum range. Although processing under these vacuum levels yields satisfactory results with regards to wetting, volatilization of alloying elements at high temperatures under reduced pressure can be a serious concern.

Oxidic cleanliness is also of paramount importance while processing high performance metals, especially superalloys and titanium with extremely high strength, high creep resistance properties at elevated service temperatures approaching the solidus temperature. Figure 2 shows the detrimental influence of increasing oxygen content on the rupture life of superalloys. Commercially pure titanium (CP Ti) has a specification of 1400 ppm maximum acceptable level of oxygen. The titanium alloy Ti-6Al-4V has specification oxygen limits in the final product ranging from 0.1% to 0.40% weight depending on the particular application. Molybdenum is classified as a "superclean" metal [3] and is typically purified by electron beam melting at 10^{-5}–10^{-6} Torr. When compared to cast or wrought product, powders have higher degree of contamination due to their much higher surface area per unit volume. As-received powders are known to harbor moisture, organics, adsorbed gases, oxide and nitride films on particle surfaces depending on the production method and shelf life. These contaminants not only inhibit successful wetting and densification of the melted powder but also degrade mechanical properties of the consolidated product. Therefore, processing under high vacuum ($< 10^{-5}$ Torr) or ultra high purity inert environments is necessary for successful direct SLS of high performance metals.

2.2 Homologous Wetting

Most of the work on wetting reported in the literature is based on isothermal wetting of dissimilar substances, *e.g.* wetting of a liquid on a solid substrate of chemical composition different than the liquid. An excellent review of the physical mechanisms governing this wetting regime is given by de Gennes [4]. The wetting behavior of a molten liquid on a substrate of its own kind was investigated only recently by Schiaffino and Sonin [5, 6, 7] This particular situation is known as "homologous wetting" and is inherently a non-equilibrium phenomenon involving simultaneous heat transfer, fluid flow and solidification.

In SLS, laser induced melting of powder and subsequent solidification onto a previously formed layer constitutes homologous wetting. Experiments were conducted by laser melting droplets onto prepared substrates of the same material to investigate homologous wetting in SLS. Stainless steel 304L was chosen as the material for investigation due to its ready availability in both powder and plate form. Stainless steel plate 0.125 inches thick was prepared by polishing with 120, 240, 400 and 600 abrasive grits, followed by $3\mu m$ diamond paste and a final polish with $0.05\mu m$ alumina slurry, followed by ultrasonic cleaning in acetone. This preparation technique was necessary to provide as clean and smooth a surface as possible since the presence of surface oxides will cause the material to spread poorly [8] and surface roughness can drastically alter wetting behavior [4].

Two types of experiments were conducted. In the first type of experiment, stainless steel powder placed on the stainless steel substrate was melted by a stationary Nd:YAG laser beam incident on the powder. In the second type of experiment, a strip of stainless steel, 1 mm wide and 4 mm long was placed on the substrate and melted by the same laser beam. Each type of experiment was conducted under high vacuum ($< 10^{-5}$ Torr) with no preheat, 350° C preheat and 900° C preheat to document the influence of preheat on the wetting behavior (analogous to the Stefan number in the studies of Schiaffino and Sonin [5]). The dynamics of melting, droplet formation, wetting and solidification were captured by video microscopy. The objective in these experiments was to visualize and qualitatively understand the wetting behavior of a metal melt on a substrate of its own kind. Therefore, no attempt was made to carefully control the temperature of the superheated melt. Such an arrangement could be implemented by controlling the laser power via feedback from a pyrometer aimed at the melt pool.

All the experiments revealed that after melting and droplet formation, the molten metal showed no tendency to spread and wet the underlying substrate. Instead, it formed a nearly spherical droplet having a point like contact with the substrate. The influence of preheat temperature on the wetting behavior was minimal and could not be distinguished visually. Sequential frames from video microscopy of one such experiment conducted with stainless steel strip on stainless steel plate is shown in Figure 3. The image at 1s shows the point of incidence of the laser beam, approximately at midlength of the strip. At 33s, the ends of the strip begin to lift off the substrate and fold in rapidly towards the center. The laser beam is turned off at 49s, revealing a very nearly spherical molten droplet and by 54s, the droplet has solidified.

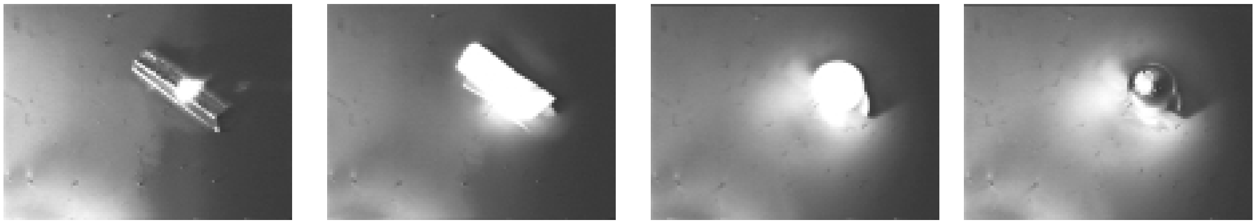

Figure 3: Homologous wetting experiment at 1s, 33s, 49s, and 54s (right).

The solidified droplets (with largest dimension typically 2mm) exhibited different shapes for powder and solid strips. In the case of "powder on plate" type experiments, the solidified droplets, shown on the left in Figure 4 had an elongated peaked feature at the top and a finite contact area with the plate. On the other hand, the solidified droplets of "strip on plate" type experiments, shown on the right in Figure 4 exhibited a much higher degree of sphericity, and a very small area of contact with the plate. The typical length scale in the photos is 2 mm.

Figure 4: Solidified droplets in "powder on plate" experiment (left) and "strip on plate" experiment (right).

Very poor metallurgical bonding was observed between the solidified droplet and the substrate in each of the homologous wetting experiments conducted on stainless steel. The solidified droplets were easily detached from their respective substrates. In addition, the substrates did not exhibit any evidence of melting at the droplet-substrate interface. Despite excellent atmosphere control (down to 10^{-6} Torr), poor wetting observed in these experiments resulted due to a lack of substrate remelting and ensuing epitaxial solidification. As shown in the following section, remelting of the underlying substrate is necessary to break down surface contamination (*e.g.* oxide films) in order to provide a clean interface at the atomic level between the solid and the liquid.

2.3 Epitaxial Solidification in Direct SLS

Direct SLS of metals is very similar to fusion welding. In fusion welding, the base metal and the weld metal may have similar but not necessarily the same composition whereas in direct SLS of monolithic metallic materials, the base metal and weld metal are necessarily the same. Some dilution of the base metal is known to occur in all types of fusion welding. Dilution refers to partial localized remelting of the base metal during welding and is necessary to provide a continuous interface free of oxide films or other contaminants between the solidifying liquid weld metal and the base metal. Dilution is deemed extremely important to ensure good weld integrity. The most important implication of dilution or "meltback" is that during solidification, grain growth will occur at the solid-liquid interface between the base metal and the liquid in contact with it. Grain growth is important because it has been well established by metallographic inspection that initial solidification in fusion welding occurs by epitaxial solidification [9]. Due to the significant similarities between fusion welding and direct SLS, it is instructive to understand the implications of epitaxial solidification on SLS process control.

Epitaxial solidification is a process of heterogeneous nucleation. In heterogeneous nucleation, a solid nucleus "nucleates" from the liquid onto a substrate with which the liquid is in contact. The shape of the nucleus is governed by the balance of interfacial free energies between the nucleus, solid and the liquid. It can be shown that the total interfacial free energy of this system is minimized when the nucleus assumes the shape of a spherical cap as shown in Figure 5.

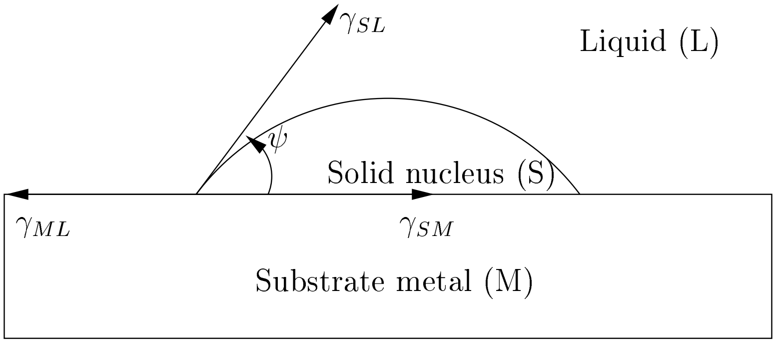

Figure 5: Heterogeneous nucleation of a solid nucleus at the solid-liquid interface.

At equilibrium, the balance of interfacial forces is given by

$$\gamma_{ML} = \gamma_{SM} + \gamma_{SL} \cos \psi \tag{2}$$

where the interfacial free energies are γ_{ML} between the substrate metal and the liquid, γ_{SM} between the solid nucleus and the substrate metal, and γ_{SL} between the solid nucleus and the liquid. The contact angle of the nucleus is ψ. Rearranging equation 2 gives

$$\cos \psi = \frac{\gamma_{ML} - \gamma_{SM}}{\gamma_{SL}} \tag{3}$$

In the context of direct SLS, the compositions of the solidified nucleus and the solid substrate are the same. Thus the interfacial energy between the nucleus and the solid substrate should be negligible while the interfacial energies between the nucleus and the liquid, and the solid substrate and the liquid should be about the same. This leads to the following approximations:

$$\begin{aligned} \gamma_{SM} &\approx 0 && (4) \\ \gamma_{ML} &\approx \gamma_{SL} && (5) \\ \psi &\to 0 && (6) \end{aligned}$$

The change in free energy associated with the formation of a solid "spherical cap" nucleus with radius of curvature r is given by

$$\begin{aligned} \Delta G_{het} &= -V_S \Delta G_v + A_S \gamma_{SL} && (7) \\ &= \left(-\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL} \right) S(\psi) && (8) \end{aligned}$$

where ΔG_v is the free energy change per unit volume associated with formation of the nucleus, V_S is the volume of the nucleus, A_S is the surface area of the new interface created between the solid nucleus and the liquid, and $S(\psi)$ is a shape factor dependent on the contact angle given by

$$S(\psi) = \frac{(2+\cos\psi)(1-\cos\psi)^2}{4} \tag{9}$$

By differentiating equation 8 with respect to r and setting the result equal to zero, the critical radius $r^\star$ to promote heterogeneous nucleation is given by

$$r^\star = \frac{2\gamma_{SL}}{\Delta G_v} \tag{10}$$

By substituting the expression for $r^\star$ into equation 8, the associated nucleation energy barrier for heterogeneous nucleation to proceed is

$$\Delta G^\star_{het} = \frac{16\pi}{3}\frac{\gamma^3_{SL}}{\Delta G^2_v}S(\psi) \tag{11}$$

It is of interest to note the dependence of $\Delta G^\star_{het}$ on $S(\psi)$. From equations 4-6, it apparent that in epitaxial solidification, $S(\psi) \to 0$. This result implies that the energy barrier for heterogeneous nucleation to proceed during epitaxial solidification is vanishingly small. This is in stark contrast to coventional casting processes in which ψ is finite, and hence $S(\psi)$ and $\Delta G^\star_{het}$ are finite due to mold and cast materials being dissimilar, as illustrated by Grong [10] in Figure 6.

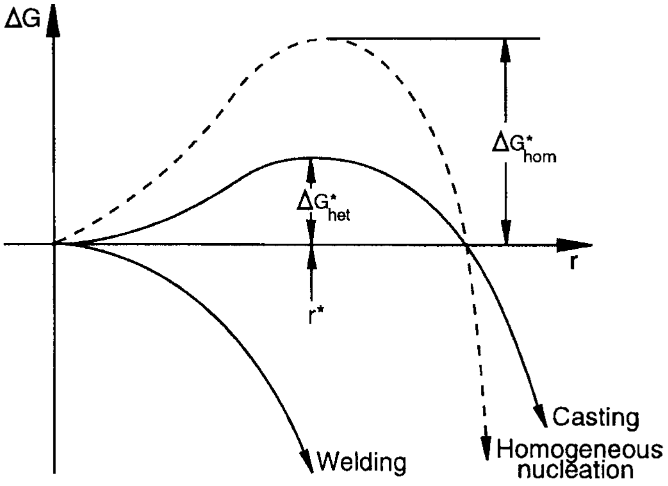

Figure 6: Schematic of free energy change associated with heterogeneous nucleation in casting and welding juxtaposed with free energy change in homogeneous nucleation (after Grong, 1994).

Nucleation proceeds immediately in epitaxial solidification by virtue of the negligible energy barrier. For this mode of solidification to occur, the substrate must be partially melted back to promote growth from the prior grains of the substrate. Epitaxial solidification by heterogeneous nucleation is indeed the mode of solidification in direct SLS processing to full density. Evidence of epitaxial solidification was confirmed by microstructural examination of sections of SLS processed material encompassing several layer thicknesses.

A cross-section of specimen 102097, shown on the left in Figure 7 is an example of incomplete homologous wetting and solidification. In this case, the melt front from above barely propagated down to the surface of the previous layer. The uniformity of layer thickness is particularly notable. In contrast, the fabricated layers in the cross-section of specimen 102497 produced at a higher laser power density, shown on the right in Figure 7, are completely indistinguishable indicating continuous grain growth across the layers. This indicates that sufficient meltback of the previous layer took place tp induce epitaxial solidification. It should be noted that these micrographs on traverse approximately three layer thicknesses.

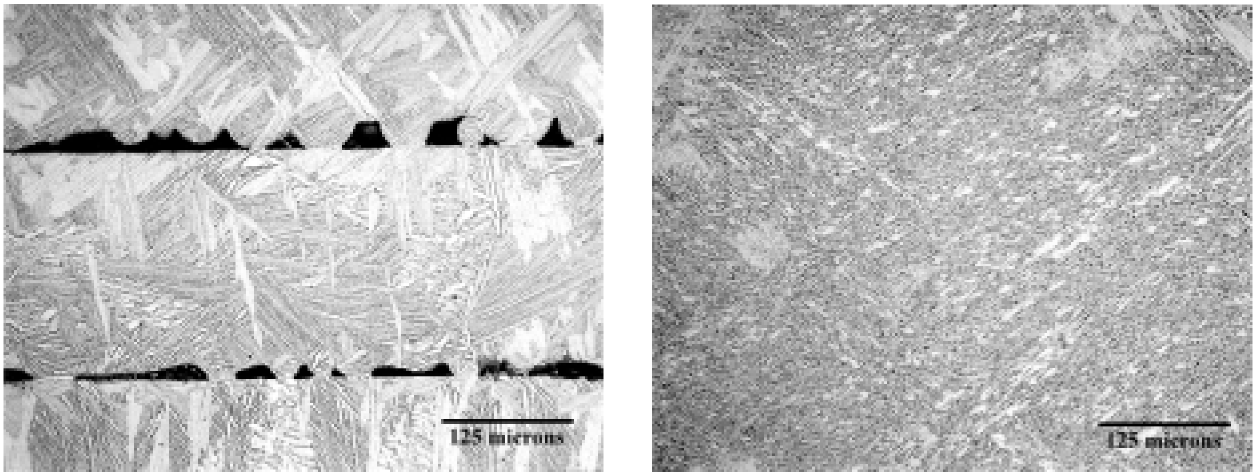

Figure 7: Etched microstructure of Ti-6Al-4V specimen 102097 (Kroll's reagent).

Another benefit resulting from epitaxial solidification is fine grain size resulting in improved mechanical properties. Equation 10 shows that for heterogeneous nucleation to proceed, the critical radius of the nucleus $r^\star$ depends on the solid-liquid interfacial free energy γ_{SL}. However, in SLS, the solid and liquid are of the same composition (assuming negligible contamination or segregation). Thus, γ_{SL} is very small implying that $r^\star$ is very small. Since SLS is a localized solidification process, this means that under identical processing conditions (temperature gradients at the solid liquid interface, cooling rates, etc), the "as SLS processed" material will exhibit finer and more uniform grain size compared to conventional casting. This hypothesis was also confirmed by examining the etched microstruture of SLS processed Ti-6Al-4V which revealed finer grain size than conventionally cast Ti-6Al-4V.

Thus, the mechanism for "good wetting" in direct SLS is epitaxial solidification by heterogeneous nucleation. As an analogue to fusion welding [9], in SLS, remelting of the previous layer is necessary to ensure full density. Remelting the previous layer removes surface contaminants, breaks down oxide films, provides a clean solid-liquid interface at the atomic level and allows epitaxial grains to grow heterogeneously. Laser processing parameters in direct SLS should be chosen so as to ensure that sufficient meltback of the previous layer takes place and continuity of the solid-liquid interface under the moving laser beam is maintained.

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