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

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3 Volatilization of Elements in Direct SLS

Volatilization of elements is a well known phenomenon in vacuum metallurgy [1], welding [2, 3], electron beam processing [4, 5] and thin film technology [6]. Evaporation and condensation of metals has been noted in direct SLS as well. The evaporation process from a metal melt is governed by four distinct regimes: mass transport of atoms from the interior of the melt to its surface, phase change to gaseous state at the surface, mass transport in the gas phase above the melt and finally condensation.

3.1 Evaporation of a Pure Metal

The molecular (or atomic) rate of evaporation per unit area and time for a liquid in equilibrium with its vapor was derived first by Hertz and later modified by Knudsen [6] to give

$$\frac{dN_e}{A_e dt} = \alpha_v \left(\frac{1}{2\pi mkT}\right)^{\frac{1}{2}} (P_v - P) \qquad (s^{-1}) \tag{1}$$

where m is mass of an individual molecule, k is Boltzmann's constant, T is the absolute temperature, P_v is the vapor pressure at the liquid's surface temperature and P is the hydrostatic pressure acting on the liquid surface. The coefficient α_v accounts for the fraction of vaporized molecules that are ejected and not resorbed back into the evaporating surface, hence, the maximum evaporation rate is attained when $\alpha_v = 1$.

Langmuir showed that the Hertz-Knudsen equation was also applicable to vaporization from free solid surfaces. In addition, he demonstrated that for pressures below 0.1 Torr ($\approx 10^{-4}$ atm), the vaporization rate is independent of residual gas pressure due to the negligible resistance offered. This resulted in the Langmuir equation for the maximum vaporization rate expressed in mass flux form as [6]

$$\Gamma = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} P_v \tag{2}$$

The Clausius-Clapeyron equation describes the change of equilibrium vapor pressure as a function of temperature and is given by

$$\frac{dP_v}{P_v} = \frac{LdT}{RT^2} \tag{3}$$

where L is the molar latent heat of vaporization and R is the molar gas constant. If the latent heat of vaporization is assumed constant for the temperature range of interest, equation 3 can be integrated to give the relation

$$P_v(T) = P_0 e^{-\frac{L}{RT}} \tag{4}$$

For most materials, in the range of vapor pressures below 1 Torr (1.315×10^{-5} atm), it has been observed experimentally [7] that the vapor pressure is indeed related to the temperature in the form of equation 4. Substituting equation 4 into equation 2 for the evaporation rate yields the form

$$\Gamma = P_0 \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{L}{RT}} \tag{5}$$

showing the near exponential dependence of the vaporization rate on the vaporization temperature.

3.2 Alloy Melting and Vaporization Under Vacuum

In the melting of alloys under vacuum, volatile solute and impurity atoms are vaporized in addition to base metal atoms. Therefore, mass transport of the solute from the interior to the surface must be considered in addition to evaporation from the surface. Both processes contribute to the overall transfer of metal atoms into the gas phase and it is therefore important to determine the rate limiting step.

The average mass transfer coefficient in an stirred metal melt is described by [8]

$$k_{m,l} = 2\left(\frac{D}{\pi\theta}\right)^{\frac{1}{2}} \tag{6}$$

where D is the diffusion coefficient (m^2/s) of the solute in the liquid and θ is the "residence time" (s), which is given by the melt pool characteristic length divided by the surface velocity of the flowing melt.

Thus, the flux to the surface from the bulk liquid is

$$j_A = k_{m,l}(C_{A\infty} - C_A^s) \tag{7}$$

where j_A is the flux (mol $m^{-2}s^{-1}$), $C_{A\infty}$ and C_A^s are volumetric concentrations of the solute in the bulk and at the surface respectively.

Evaporation from the surface of a pure metal was described earlier. In the case of an alloy, the evaporation rate or flux of an alloying component is given by [8]

$$j_A = \frac{\gamma_A P_A^0 C_A^s}{\rho\sqrt{2\pi MRT}} \tag{8}$$

where γ_A is the activity coefficient of the component, P_A^0 is the vapor pressure of the pure component at the temperature under consideration, ρ is the molar density of the alloy and M is the alloy's molecular weight. From equation 8, the mass transfer coefficient for surface evaporation is

$$k_{m,e} = \frac{\gamma_A P_A^0}{\rho\sqrt{2\pi MRT}} \tag{9}$$

When the melting and vaporization takes place under vacuum better than 0.1 Torr, the resistance to mass transport in the gas phase is negligible, as was indicated earlier. Under this condition, the liquid phase mass transfer and evaporation fluxes are in equilibrium. Therefore,

$$k_{m,l}(C_{A\infty} - C_A^s) = k_{m,e}C_A^s \tag{10}$$

Subsituting for C_A^s from equation 10 into equation 7, the expression for the flux is given by

$$\begin{aligned} j_A &= \left(\frac{k_{m,e}k_{m,l}}{k_{m,l} + k_{m,e}}\right) C_{A\infty} \qquad (11) \\ &= KC_{A\infty} \qquad (12) \end{aligned}$$

where K is the overall mass transfer rate constant which can be rewritten as

$$\frac{1}{K} = \frac{1}{k_{m,l}} + \frac{1}{k_{m,e}} \tag{13}$$

By evaluating the magnitudes of the "resistances" $\frac{1}{k_{m,l}}$ and $\frac{1}{k_{m,e}}$ offered by each step, once can determine whether they are the same order of magnitude or one is clearly the rate limiting step. The higher the degree of stirring or convection in a melt, the higher the value of $k_{m,l}$ and the smaller its effect on the overall mass transfer rate. Conversely, the lower the vapor pressure P_A^0 of the solute, the smaller the value of $k_{m,e}$ and the greater the resistance offered by surface evaporation to mass transport.

For example, it has been reported [5] that for electron beam processing of a wide variety of liquid metal systems, $k_{m,l}$ falls in the range $1\times10^{-4} - 5\times10^{-4}$ m/s. In the refining of silver from liquid copper at 1920 K by electron beam melting in a water cooled hearth, the rate constants reported were $k_{m,e} = 6.1\times10^{-4}$ m/s, $K = 1.4\times10^{-4}$ m/s to yield $k_{m,l} = 1.9\times10^{-4}$ m/s. Given that the hearth area was 0.16 m^2 and typical surface velocity observed in this experiment was 7×10^{-2} m/s, the residence time θ is of order $3s$. This value is of the order of the time expected in an inductively stirred melt [8]. If this system is considered for full density SLS processing (where a continuous melt pool would be maintained), as a first approximation we can assume that the laser scan speed is representative of the surface velocity in the melt pool and the melt pool size is on the order of the beam diameter. For a typical scan speed of 5.08 cm/s (2 in/s) and a beam diameter of 0.05 cm, the value of θ is 0.01s. Due to the high surface velocity for the pool size under consideration, it is expected that stirring is even more vigorous in SLS and that $k_{m,l,SLS} \approx 10k_{m,l,EB}$. This calculation is based on a very conservative estimate of flow velocity at the pool surface. Surface velocities induced by surface tension gradients that are 2 to 3 orders of magnitude higher than the velocity of the moving heat source have been observed and predicted [3]. This indicates very good mixing in the melt pool and that the rate limiting step for mass transfer is volatilization at the pool surface.

Evaporation of alloying elements from the melt pool also causes loss of input laser power. The power loss due to evaporation of an alloying element is given by [2]

$$P_{L,A} = \Gamma_A (L_A - \Delta H_A) \tag{14}$$

where $P_{L,A}$ is the power lost due to evaporation of element A, Γ_A is the evaporation rate of element A, L_A is the heat of vaporization of pure component A and ΔH_A is the partial molar heat of mixing of A in the alloy. The evaporative power loss affects the peak temperature attainable in the melt pool.

3.3 Vaporization Characteristics of Elements Relevant to SLS

Empirical data obeying the form of equations 4 and 5 have been used by Dushman [7] to tabulate data for a wide variety of elements. The vapor pressure data for selected elements of relevance to SLS are shown in Table 1.

Element	T_m (° C)	T_b (° C)	Vaporization Temperature (° C) At Pressure (Torr)					
			10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
Al	659	2447	882	972	1082	1207	1347	1547
B	2027	3927	1687	1827	1977	2157	2377	2657
Co	1495	2877	1162	1262	1377	1517	1697	1907
Cr	1903	2665	1062	1162	1267	1392	1557	1737
Cu	1084	2578	942	1032	1142	1272	1427	1622
Fe	1539	2857	1107	1207	1322	1467	1637	1847
Mg	650	1104	287	330	382	442	517	612
Mn	1244	2051	697	767	852	947	1067	1227
Mo	2577	4827	1987	2167	2377	2627	2927	3297
Ni	1452	2839	1142	1247	1357	1497	1667	1877
Pb	328	1751	487	551	627	719	832	977
Si	1415	2787	1177	1282	1357	1547	1717	1927
Ti	1660	3287	1321	1431	1558	1703	1877	2083
V	1857	3377	1432	1551	1687	1847	2037	2287
W	3377	5527	2547	2757	3007	3297	3647	n/a
Zn	420	906	208	246	290	342	405	485
Zr	1852	4405	1837	2002	2187	2387	2647	2977
T_m=Melting point T_b=Normal boiling point								

Table 1: Vaporization temperature of selected elements as a function of pressure.

Some important observations can be made in this table with regard to SLS process control. For example, in the $10^{-4} - 10^{-5}$ Torr vacuum range, all elements in the table except Al and Pb have vaporization temperature lower than their respective melting points. Hence, all these elements will show a very high tendency to vaporize when processed under this vacuum range. The vaporization temperature approaches and exceeds the melting point in the $10^{-2} - 10^{-3}$ Torr range. In the $1 - 10^{-1}$ Torr range, most vaporization temperatures are in excess of the melting points but not significantly. This range allows melt superheat by a few hundred degrees Centigrade before the vaporization temperature is attained. However, it should be noted that even at 1 Torr, Cr, Cu, Mg, Mn will all vaporize. Therefore, it is apparent that to inhibit vaporization, SLS processing under partial pressure rather than high vacuum is necessary.

3.4 Partial Pressure Processing—Reducing Mean Free Path

Volatilization of alloying elements has been observed during SLS processing under high vacuum. The most deleterious effect of this phenomenon is condensation of volatilized elements on the laser window, severely affecting consistency of laser energy delivery. Condensation of volatilized elements also takes place on chamber interior surfaces that can cause contamination during subsequent processing of other materials. Volatilization can also cause depletion of alloying elements resulting in alteration of alloy chemistry.

In the absence of laser spot temperature control so as to regulate the temperature of the melt zone, some degree of superheat is likely to occur. Therefore, it is necessary to select the operating pressure based on the elemental constituents that have the highest vaporization tendency. In order to maintain purity of the processing atmosphere, this entails evacuating the chamber to high vacuum followed by back fill to partial pressure with an ultrahigh purity inert gas such as 99.999% purity Argon or Helium ($<$ 2 ppm oxygen, $<$ 3 ppm moisture, $<$ 1 ppm hydrocarbons and $<$ 6 ppm nitrogen [9]). It is necessary implement inert gas partial pressure processing to decrease the mean free path of gaseous element atoms so that condensation on the laser window is inhibited. In addition, if a continuous flow of inert gas is maintained to provide “dynamic” partial pressure processing, volatilized material will tend to be flushed away from the processing zone and out of the vacuum system.

The mean free path is defined as the average distance between successive collisions of gaseous molecules and is given by [6]

$$\lambda = \frac{kT}{\sqrt{2}P\pi\sigma^2} \tag{15}$$

where k is Boltzmann’s constant, T is the absolute temperature, P is the pressure and σ is the molecular diameter. Assuming $\sigma = 5$ Å, $T = 298K$ and P is expressed in Pa, equation 15 reduces to

$$\lambda = \frac{3.642 \times 10^{-3}}{P} \quad (m) \tag{16}$$

Table 2 shows the mean free path as a function of pressure over 10 decades. Upon inspection of table 2, the reason for substantial condensation of elemental volatiles on the laser window is clear. The distance, r, from the laser window to the scanned powder surface is typically less than 0.5 m. At 10^{-7} Torr, the mean free path is about 35 m. Therefore, at 10^{-7} Torr vacuum levels, volatilized metal atoms travel unimpeded to the laser window and processing chamber walls. At an order of magnitude lower vacuum, *i.e.* 10^{-6} Torr, the mean free path of 3.59 m is still an order of magnitude larger than r. It is only at 10^{-5} Torr that the mean free path is of same order of magnitude as r. Thus, if the arrival rate of volatilized metal

Pressure (atm)	Pressure (Torr)	λ (m)
1	760	3.59×10^{-8}
10^{-1}	76	3.59×10^{-7}
10^{-2}	7.6	3.59×10^{-6}
10^{-3}	7.6×10^{-1}	3.59×10^{-5}
10^{-4}	7.6×10^{-2}	3.59×10^{-4}
10^{-5}	7.6×10^{-3}	3.59×10^{-3}
10^{-6}	7.6×10^{-4}	3.59×10^{-2}
10^{-7}	7.6×10^{-5}	3.59×10^{-1}
10^{-8}	7.6×10^{-6}	3.59
10^{-9}	7.6×10^{-7}	35.9

Table 2: Mean free path for various pressures.

atoms at their condenation on the laser window is to be substantially curtailed, it is necessary to operate at still higher pressure levels. We assume that the arrival rate is substantially reduced by decreasing the mean free path to two orders of magnitude lower than r. This hypothesis suggests that the desired operating vacuum (pressure) level is in the neighborhood of 7.6×10^{-3} Torr. This hypothesis was indeed confirmed by experiment. While substantial condensation was observed at 10^{-4} Torr partial pressure processing, condensation on the laser window was nearly completely eliminated at 10^{-3} Torr levels, allowing the fabrication of large complex parts spanning several hundred layers and several tens of hours build time.

3.5 Alloy Melt Refining by Evaporation of Suboxides

Melting of high performance alloys under high vacuum or ultrahigh purity inert gas partial pressure enviroments can provide the added benefit of alloy refinement by volatilization of oxides, impurities and non-metallic inclusions. Refining of alloy melts during SLS processing under vacuum can occur by mechanisms very similar to those in vacuum induction melting (VIM), vacuum arc remelting (VAR) and electron beam cold hearth refining (EBCHR). The techniques VIM, VAR and EBCHR are presently well established for production of aerospace and specialty alloys including nickel base superalloys and alloys of titanium [10]. From the perspective of SLS process control, it is important to consider the refining mechanisms and their impact on the chemistry of the processed material.

If the stoichiometric form of the metal oxide is M_xO_y, then the atomic ratio of oxygen to metal in the vapor is given by

$$\frac{O}{M} = \frac{\Sigma y P_{M_xO_y}}{\Sigma x P_{M_xO_y}} \tag{17}$$

where P is the partial pressure of the M_xO_y gaseous species.

The oxygen to metal ratio in the metallic phase is defined as the ratio of mole fractions of oxygen and metal. At low concentrations of oxygen, this ratio reduces to the mole fraction X_0 of oxygen in the metal. The ratio R is defined as [11]

Element	Evaporating oxide	T (K)	P_M (atm)	X_0 (sat)	R (low X_0)
Oxygen alloys of 4th group metals					
Si	SiO	1685	$10^{-6.3}$	$10^{-3.7}$	10^{8}
Ge	GeO	1210	10^{-9}	$10^{-2.5}$	$10^{9.5}$
Sn	SnO	1000	10^{-10}	10^{-2}	$10^{6.3}$
Pb	PbO	1000	$10^{-4.8}$	$10^{-3.1}$	$10^{2.6}$
Oxygen alloys of transition metals					
Ti	TiO	1940	$10^{-5.2}$	0.3	1
V	VO	2190	$10^{-4.4}$	0.3	10
Cr	CrO	2171	$10^{-2.2}$	10^{-2}	$10^{0.5}$
Mn	MnO	1516	$10^{-2.8}$	10^{-2}	10^{-4}
Fe	FeO	1810	$10^{-4.5}$	$10^{-2.2}$	$10^{0.4}$
Co	CoO	1765	$10^{-5.1}$	$10^{-2.1}$	10
Ni	NiO, O	1726	$10^{-5.4}$	$10^{-2.1}$	10
Oxygen alloys of refractory metals					
Zr	ZrO	2125	$10^{-7.7}$		10
Nb	NbO	2740	$10^{-5.8}$		10^{3}
Mo	Mo_3O_9, MO_3, MO_2, O	2880	$10^{-4.3}$		10^{6}
Ta	TaO	3250	10^{-5}		10^{5}
W	W_3O_9, WO_3, WO_2, O	3650	10^{-4}		10^{6}

Table 3: Vaporization behavior of selected elements, after Brewer and Rosenblatt (1962).

$$R = \frac{\left(\frac{O}{M}\right)_{vapor}}{\left(\frac{O}{M}\right)_{metal}} \tag{18}$$

If $R > 1$, vaporization of the metal phase will lower the oxygen content of the base metal. Brewer and Rosenblatt [11] state that substantial purification (>50%) will only occur if $R > 10$ since for $R = 10$, vaporization of 10% of the metal results in 50% reduction of oxygen impurity. Their data for various metals is shown in Table 3.

Inspection of Table 3 reveals that the elements Si, Ge, Pb and Sn will undergo high purification by evaporative loss of oxide. However, the second group of metals which are of most interest to SLS (consituents of steel, titanium and alloys) will not undergo substantial deoxidation. Therefore, in order to meet specifications on the chemistry of such alloys while processing by SLS under vacuum or ultrahigh purity inert gas partial pressure environments, it is important to monitor not only the initial chemisty of the feedstock material but also the leak integrity of the processing environment to prevent further contamination. On the other hand, the refractories except Zr all have very high values of R and will thus undergo very good purification.

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