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Title: Powder Bed Charging during Electron-Beam Additive Manufacturing

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Abstract: Electrons injected into the build envelope during powder bed electron-beam additive manufacturing can accumulate on the irradiated particles and cause them to repel each other. Under certain conditions, these electrostatic forces can grow so large that they drive the particles out of the build envelope in a process known as “smoking”. In the present work, we investigate the causes of powder bed charging and smoking during electron-beam additive manufacturing. In the first part of the paper, we characterize the surface chemistry of a common feedstock material—gas-atomized Ti-6Al-4V powder—and find that a thick, electrically insulating oxide overlayer encapsulates the particles. Based on these experimental results, we then formulate an analytical model of powder bed charging in which each particle is approximated as a capacitor, where the particle and its substrate are the electrodes and the oxide overlayer is the dielectric. Using this model, we estimate the charge distribution in the powder bed, the electrostatic forces acting on the particles, and the conditions under which the powder bed will smoke. It is found that the electrical resistivity of the oxide overlayer strongly influences the charging behavior of the powder bed and that a high resistivity promotes charge accumulation and consequent smoking. This analysis suggests new quality control and process design measures that can help suppress smoking.

Keywords: additive manufacturing, electron beam welding, powder processing, surface spectroscopy, electrostatics

1. Introduction

Powder bed electron-beam additive manufacturing uses a high-power electron beam (e-beam) to fuse powder feedstock, layer-by-layer, into bulk objects. Under certain conditions, the electrons injected into the feedstock by the e-beam can accumulate on the irradiated particles, causing them to electrostatically repel each other. In extreme cases, these electrostatic forces can grow so large that they eject the particles from the powder bed in a process termed “smoking” [1, 2]. Smoking is generally undesirable because it can cause build failure.

Methods to suppress smoking have traditionally been developed through trial-and-error optimization, guided by independent experimental observations and qualitative rules of thumb. One such guideline is that increasing the temperature of the build envelope often makes powders less susceptible to smoking. Another useful rule of thumb is that coarse powders are typically more resistant to smoking than fine powders. In addition, we have found that smoking will not occur during the melt operation if it does not occur during the preceding pre-heat operation. However all of these heuristics lack physical explanations and are therefore not always useful for predicting whether a given parameter set will suppress smoking.

A basic understanding of the powder feedstock's charging behavior is required to accurately predict those parameter sets that will give rise to smoking. One feature of the powder that strongly influences its charging behavior is its surface chemistry, as this determines the electrical properties of the junctions that the particles form with their surroundings [3-6]. Specifically, particles encapsulated by an electrically insulating oxide overlayer will tend to accumulate charge because this oxide overlayer can inhibit charge redistribution across particle contacts. While it is known that the nickel and titanium alloys commonly used in e-beam additive manufacturing grow native oxides when they are in bulk form [7-12], the structure and properties of the oxides that they develop in powder form have not been characterized to the best of our knowledge.

In this work, we use both experiments and theory to investigate the causes and consequences of powder bed charging during e-beam additive manufacturing. Experimentally, we utilize surface characterization techniques to show that a common e-beam additive manufacturing feedstock material—gas-atomized Ti-6Al-4V powder—is covered by an electrically insulating oxide overlayer. We then formulate an analytical model of powder bed charging that is based on this “core-shell” particle structure, and that can guide the selection of process parameters to suppress smoking.

2. Experimental Methods

We used X-ray photoelectron spectroscopy (XPS) to characterize the surface chemistry of commercial Ti-6Al-4V, wt% powders prepared by the hydride-dehydride process (Reading Alloys) and by inert gas atomization (TLS Technick GmbH & Co). The quenching medium used in the inert gas atomization process was argon. The nominal compositions of the powders are summarized in Table 1. We focused on Ti-6Al-4V in this study because this alloy is susceptible to smoking and it is a common feedstock material in e-beam additive manufacturing. The powder prepared by gas atomization was of interest because the majority of Ti-6Al-4V powder feedstock is made with atomization processes, while the powder prepared using the hydride-dehydride technique was of interest because these powders are reported to have low oxygen contents. Both powders had particle size distributions that ranged from 40 to 130 μm , which is standard for e-beam additive manufacturing feedstock. The gas-atomized particles were spherical, whereas the hydride-dehydride particles were irregularly shaped.

We performed the XPS measurements on a Thermo Scientific Model K-Alpha XPS instrument that uses monochromatic Al K_{α} x-rays (1486.6 eV). We prepared samples by spreading Ti-6Al-4V powders on double-sided tape attached to a glass slide, using sufficient powder to completely hide the underlying tape. We acquired two sets of spectra from each sample: one set from the as-received powders and another set after sputter etching the powders for 2 minutes using 3 kV argon ions. Because the powders were mounted on glass slides, we used a charge neutralization flood gun to maintain stable analysis

conditions. The flood gun uses a combination of low energy electrons and argon ions for optimum charge compensation. The pressure in the analysis chamber with the flood gun operating was 2×10^{-7} mbar. We collected wide energy range survey spectra (0-1350 eV) using an analyzer pass energy of 200 eV and an energy step size of 1 eV, as well as core level spectra over a narrow energy range using an analyzer pass energy of 50 eV and a 0.1 eV step size.

3. Results and Discussion

Figure 1 shows the survey spectra for the as-received and sputter-etched powders. We used these spectra to calculate the compositions of the as-received and etched surfaces, and these results are summarized in Table 2.

Table 2 reveals two important features of the as-received powders. First, there was a much higher oxygen content in the as-received surfaces than in the etched surfaces, indicating both the hydride-dehydride and gas-atomized powders had heavily oxidized overlayers. Second, the surface of the gas-atomized powder was enriched in aluminum relative to the parent metal: the ratio of aluminum to titanium atoms in the surface of the gas-atomized powder was 0.6 while the expected ratio for Ti-6Al-4V is 0.1. A possible explanation for this aluminum enrichment is that the aluminum segregated to the oxygen-rich surface of the particle during atomization because it has a higher affinity for oxygen than either vanadium or titanium [13]. That this aluminum-enrichment is only observed in the gas-atomized powder is most likely because the aluminum can rapidly diffuse to the particle surface during the high-temperature atomization process, but not the low-temperature hydride-dehydride process.

Figures 2a-c compare the $Ti2p_{3/2}$, $Al2p$, and $V2p_{3/2}$ spectra for the as-received and sputter-etched materials. In the as-received spectra, the $Ti2p_{3/2}$ peak is assigned to Ti^{4+} cations ($Ti2p_{3/2}$ 458.6 eV [14, 15]), and the $Al2p$ peak is indexed to Al^{3+} cations ($Al2p$ 74.7 eV [16]). The $V2p_{3/2}$ peak is also associated with an oxidized species ($V2p_{3/2}$ 516.5 eV [16]), though its exact valence state is difficult to determine because of the broad nature of the vanadium peak. In general, sputtering is seen to remove features attributed to metal-oxygen bonding and to increase the metallic signals, confirming the presence of an overlayer composed mainly of titanium- and aluminum-oxides.

The spectra from the as-received materials in Figure 2a feature low-intensity, metallic titanium signals ($Ti2p_{3/2}$ 453.7-454.1 eV [17, 18]) that originated from the core of the particles. The integrated intensities of the oxidized and metallic titanium signals in these spectra can be used with a formalism developed by Nyborg *et al.* to estimate the thickness of the oxide overlayer covering the particles [19]. Accordingly, we estimate that the oxide overlayer was roughly 3 nm thick for both the gas-atomized and hydride-dehydride powders.

The C1s and O1s spectra for the as-received and sputtered samples are shown in Figures 2d and 2e. The C1s spectra show that the carbon signal from the as-received surface is due to adventitious, surface adsorbed carbon-containing species, possibly introduced by the tape, while the carbon signal from the sputtered surface is due mainly to carbon-metal bonding (C1s 280.8-283 eV [16]). The intensity of the O1s signal is seen to decrease significantly with sputtering, though there is still a sizeable O1s peak in the spectra of the etched material that suggests oxygen-metal bonding (O1s 528-531 eV [16]).

Comparison of the oxide overlayer found on these Ti-6Al-4V powders with the native oxide found on bulk Ti-6Al-4V parts reveals some similar features. For example, several investigators have reported that the native oxide on bulk Ti-6Al-4V specimens is rich in aluminum but deficient in vanadium [10-12, 20], which matches the concentration gradient found on the surface of the gas-atomized particles. However, an important difference between the overlayers found on the bulk and on the particulate materials is their respective thicknesses—the oxides on both the hydride-dehydride and gas-atomized particles appear to be at least twice as thick as the native oxide typically found on bulk specimens [12]. Other studies on the surface chemistry of gas- and water-atomized powders have also reported thick oxide overlayers [21-28], so this appears to be a common feature of atomized powders. However, the presence of a thick oxide overlayer on the hydride-dehydride particles is somewhat surprising, given the fact this technique is supposed to minimize oxygen pick-up.

The oxide overlayers on both the gas-atomized and hydride-dehydride powders are so thick that there is a vanishingly small probability of electrons tunneling through them [29, 30]. Consequently the resistivity of these overlayers should approach those of bulk oxides with the same composition and structure. While metal-oxides can exhibit a range of resistivities, many of the engineering materials used in e-beam additive manufacturing develop scales that contain phases which are either semiconducting or insulating. For instance, the oxide overlayer on these Ti-6Al-4V powders is likely composed of Al_2O_3 and TiO_2 , and both of these compounds have high electrical resistivities at room temperature [31, 32]. Similarly, the chromium-bearing nickel-based superalloys used in e-beam additive manufacturing grow oxide overlayers composed of Cr_2O_3 , NiO , and a $\text{Ni}(\text{Cr,Fe})_2\text{O}_4$ spinel [7], all of which are semiconductors, with resistivities that are typically many orders of magnitude greater than that of the base metal [33, 34]. As alluded to above, these insulating oxide overlayers are especially important in the context of e-beam additive manufacturing, since they can inhibit charge dissipation, and consequently make the powder bed more susceptible to smoking. In the following, we develop a model of powder bed charging based on this “core-shell” particle structure.

4. Powder Bed Charging

We now turn our attention to the charge distribution that develops in the build envelope during e-beam additive manufacturing. The electrons that impinge on the powder bed strike the feedstock material at three different stages of processing: (1) loose powder particles that have been spread across the top of the build envelope, (2) fully dense material, and (3) partially sintered material that surrounds the fully dense material. Figure 3 is a schematic of the powder bed that shows these three materials in cross-section. Roughly 70% of the incident electrons strike the loose powder layer because it contains ~ 1 layer of particles with a 2D-projected area fraction of 0.7. Since the mean penetration depth of 60 keV electrons into most oxides and metals is on the order of microns (i.e., three orders of magnitude greater than the thickness of the oxide overlayer), essentially all of these electrons come to rest in the metallic core of the particles. The electrons that pass between the particles are subsequently blocked by either the partially sintered or fully-dense materials. The partially sintered and fully-dense materials are electrically grounded and have a high electrical conductivity, thus the electrons that they absorb are rapidly diverted to ground. The loose powder particles, on the other hand, can be electrically insulated from their surroundings if they are covered with an oxide overlayer like that found on the Ti-6Al-4V powder. In this case, the particles can accumulate significant charge because electrons must redistribute across the oxide overlayer for the charge to dissipate, and the timescales associated with this process can be large.

To calculate the charge on one of these powder particles, we treat the junction between the particle and its substrate as a capacitor, where the particle and the substrate are the electrodes, and the oxide is the dielectric, as depicted in Figure 4. Under this approximation, the charge Q on a particle at time t can be calculated by solving the initial value problem

$$\frac{dQ}{dt} + \frac{Q}{\tau} = I(t) \quad (1a)$$

$$Q(0) = Q_0 \quad (1b)$$

where Q_0 is the initial charge on the particle, τ is a time constant associated with charge dissipation across the dielectric, and $I(t)$ is a function of time that describes the electric current injected into the particle by the e-beam. The charge dissipation time constant τ equals the product of the permittivity and the resistivity of the oxide overlayer, assuming it is an ohmic resistor [35]. The value of τ can range from picoseconds to days, depending on the temperature of the powder bed, the microstructure of the overlayer, and the composition of the overlayer [36, 37]. For very thin overlayers, the thickness of the overlayer can also affect τ because of electron tunneling.

We first use Eqs 1a and 1b to analyze the charging behavior of an isolated, initially neutral particle that is irradiated by a stationary e-beam with a uniform current density J for a time Δt , beginning at $t = 0$. The beam is assumed to be collimated, to completely span the particle, and to be absorbed with an efficiency η so that

$$I(t) = \begin{cases} J\pi R^2 \eta & 0 \leq t \leq \Delta t \\ 0 & \text{otherwise} \end{cases}. \quad (2)$$

where R is the radius of the particle. Combining Eq 2 with Eq 1a, setting $Q_0 = 0$, and solving for $Q(t)$ gives

$$Q(t) = \begin{cases} 0 & t < 0 \\ J\pi R^2 \eta \tau \left(1 - e^{-\frac{t}{\tau}}\right) & 0 \leq t < \Delta t \\ J\pi R^2 \eta \tau \left(1 - e^{-\frac{\Delta t}{\tau}}\right) e^{-\frac{t}{\tau}} & \Delta t \leq t \end{cases}. \quad (3)$$

Next we adapt this result to describe the steady-state charge distribution that develops in an initially neutral row of particles irradiated by an e-beam traveling along the row with a constant velocity v . We maintain our previous assumptions that the e-beam spans the particles and has a uniform current density. In addition, we assume that the particles are spherical, are monodisperse, and have an appreciably smaller diameter than the e-beam diameter, which is often true in practice. We also define the coordinate system such that the e-beam travels along the x -axis in the positive x -direction, and the leading edge of the e-beam passes through the origin at $t = 0$. In this case, for a particle whose left-most edge is at position x , $I(t)$ is

$$I(t) = \begin{cases} J\pi R^2 \eta & \frac{x}{v} \leq t < \frac{x}{v} + \Delta t \\ 0 & \text{otherwise} \end{cases}. \quad (4)$$

Here Δt is the time it takes the beam to pass over the particle, which can be estimated as

$$\Delta t = \frac{kD}{v} \quad (5)$$

with D the beam diameter and k a constant of order unity that accounts for the position of the particle relative to the center of the beam. In an Arcam e-beam system, D ranges from 0.2 to 2 mm and v varies between 0.5 and 10 m/s so that the order of Δt can range from 0.01 to 1 ms.

Because of the similarities between Eqs 2 and 4, Eq 3 can be modified by replacing the variable t with $t - \frac{x}{v}$ and by eliminating Δt with Eq 5 to yield an expression for the charge distribution in the row of irradiated particles:

$$Q(x, t) = \begin{cases} 0 & t < \frac{x}{v} \\ J\pi R^2 \eta \tau \left(1 - e^{-\frac{t}{\tau} + \frac{x}{v\tau}}\right) & \frac{x}{v} \leq t < \frac{x}{v} + \frac{kD}{v} \\ J\pi R^2 \eta \tau \left(1 - e^{-\frac{kD}{v\tau}}\right) e^{-\frac{t}{\tau} + \frac{x}{v\tau}} & \frac{x}{v} + \frac{kD}{v} \leq t \end{cases}. \quad (6)$$

Accordingly, the maximum charge on any particle in the row is

$$Q_{\max} = J\pi R^2 \eta \tau \left(1 - e^{-\frac{kD}{v\tau}}\right). \quad (7)$$

Eq 6 can be used to calculate the charge distribution in the top-most layer of particles in the powder bed when it is combined with a function that describes the beam shape.

Figure 5 shows the charge distribution that develops in a row of particles whose centers are coincident with the x-axis so that $k = 1$. In this Figure, the x-coordinate and charge have been normalized by D and $J\pi R^2\eta\Delta t$ respectively. The shaded region indicates the instantaneous position of the e-beam, which is traveling from left to right. We calculated the three curves shown in Figure 5 using different values of the dimensionless group $v\tau/D$ —0.1, 3, and 10. This dimensionless group is the ratio of the charge dissipation time constant to the time each particle spends under the beam. Inspection of the curves shows that the maximum charge increases with decreasing $v\tau/D$, other parameters being held constant, and that the charged regions extend a distance of order $v\tau/D$ behind the e-beam. This relationship between the tail length and $v\tau/D$ makes intuitive sense because when this ratio is large, the particles retain their charge long after the beam has passed over them.

These results describe the charging behavior during the melt operation, where the beam passes over a particle once. In contrast, during the pre-heat operation, the beam will raster across the same particle multiple times so that $I(t)$ becomes periodic, with a period T that equals the time required for the beam to raster across the area being pre-heated. This period is

$$T = \frac{L}{v} \quad (8)$$

where L is the product of the raster length and the number of hatches in the pre-heated area. There are therefore three important timescales associated with Eq 1 during pre-heating— τ , Δt , and T associated with the charge dissipation, beam-particle interaction, and rastering processes, respectively. The relative magnitudes of these timescales largely determine the charge that accumulates on the particles. While the ratio $\Delta t/T$ is always much less than unity because D is always much smaller than L , the ratios τ/T and $\tau/\Delta t$ can take on values greater or less than unity, depending on the value of τ . If the ratio τ/T is much smaller than unity, then the charge injected into a particle during a single pass of the e-beam completely dissipates before the next pass, and the charging behavior is similar in form to that during the melting operation. On the other hand, when τ/T is large, charge accumulates with each pass of the e-beam. To calculate the charge on a particle in this second regime, $I(t)$ can be approximated as a series of delta functions with magnitude $J\pi R^2\eta\Delta t$ and period T :

$$I(t) = J\pi R^2\eta\Delta t \sum_n \delta(t - nT). \quad (9)$$

where n is an integer. For an initially neutral particle, this form of $I(t)$ gives a charging profile like that shown in Figure 6, where there is an initial transient, after which $Q(t)$ enters a cyclic stationary state. In this cyclic stationary state, $Q_{\max}$ is given by the sum of a geometric series:

$$Q_{\max} = \sum_{n=0}^{\infty} J\pi R^2 \eta \Delta t e^{-\frac{nT}{\tau}} = J\pi R^2 \eta \Delta t \left(\frac{1}{1-e^{-\frac{T}{\tau}}} \right). \quad (10)$$

Replacing the pre-factor in Eq 10 with Eq 7, we arrive at a function that describes the full spectrum of charging behaviors during pre-heating:

$$Q_{\max} = J\pi R^2 \eta \tau \left(\frac{1-e^{-\frac{\Delta t}{\tau}}}{1-e^{-\frac{T}{\tau}}} \right). \quad (11)$$

In Figure 7, a normalized form of Eq 11 is plotted as a function of $\tau/\Delta t$ assuming $T/\Delta t = 10^3$, which is typical for a build area of order 1 cm^2 and a hatch spacing of $200 \text{ }\mu\text{m}$. The curve can be divided into three distinct regions, as indicated. In Region 1 ($\tau < \Delta t$), the charging behavior is identical to that during the melt operation. In Region 2 ($\Delta t < \tau < T$), $Q_{\max}$ is insensitive to changes in τ . Finally, in Region 3 ($T < \tau$), the charge is unable to dissipate in the interval between beam passes, and $Q_{\max}$ further increases with τ . Figure 7 shows that $Q_{\max}$ can vary over many orders of magnitude due to changes in τ alone. What ultimately limits $Q_{\max}$ is the onset of either smoking or particle melting.

5. Electrostatic Forces

We can use the results from the preceding section to estimate the charge distribution in the powder bed and the resulting electrostatic forces. As examples, Figures 8a and 8b show the charge distribution in a close-packed layer of monodisperse powder particles irradiated by a circular, collimated e-beam traveling from left to right. We calculated these charge distributions by convolving Eq 6 with a function that describes the shape of the e-beam. The instantaneous position of the e-beam is indicated by the dashed circle, and the color of the particles corresponds to their normalized net charge. The minimum separation between the particles is assumed to be twice the thickness of their oxide overlayer. The values of $v\tau/D$ used to calculate each of these charge distributions are shown, and the effects of $v\tau/D$ on the charge distribution are seen to parallel those in Figure 3 (Figure 3 is essentially a cross-section of the 2D particle map shown here). To a good approximation, Figures 8a and 8b illustrate the charge distribution that develops in the top-most layer of particles in the powder bed during the melt operation.

We calculated the electrostatic forces acting on the particles in Figures 8a and 8b by taking the negative gradient of the global electrostatic energy U with respect to each particle's position. We evaluated U using

$$U = Q^T P Q \quad (12)$$

where Q is a column vector whose elements are the net charges on the particles and P is a square matrix whose elements are potential coefficients. We calculated P by inverting a capacitance matrix, which we generated using the superposition principle and the approximate formulae for the capacitance between two conducting spheres given by Banerjee and Levy [38]. The only inputs needed to calculate P are the

particles' radii R , their positions, and the permittivity of the space surrounding the particles, which we assume is under vacuum.

The arrows in Figures 8a and 8b show the electrostatic forces acting on the particles. The arrow lengths correspond to the relative magnitudes of the electrostatic forces, and they have been normalized so that only comparisons within each Figure are valid. Figures 8a and 8b show that the largest forces point in a direction roughly orthogonal to the beam's travel direction, and that increases in $v\tau/D$ cause the electrostatic forces to extend behind the e-beam. Figures 8a and 8b also demonstrate how the charged particles are mostly repelled from the beam, while the uncharged particles are attracted to the beam. The uncharged particles can be attracted to the beam even though they have no net charge because they are conductors, and they can therefore develop an electric dipole moment as a result of the charged particles in their vicinity. An important consequence of the ability of the uncharged particles to develop a dipole moment is that uncharged particles far removed from the beam still experience electrostatic forces. This is likely why smoking often involves a region of the powder bed much larger than the beam diameter.

For predicting smoking events, we are primarily concerned with the magnitude of the largest electrostatic force in the powder bed. Because the electrostatic forces are dominated by nearest neighbor interactions, we can estimate the magnitude of this force by considering two contacting particles. Following Banerjee and Levy, the electrostatic force F_Q between identical, conductive, spherical particles with oxide overlayers can be approximated as

$$F_Q = \frac{Q^2}{16\pi\epsilon_0 R^2} \times g\left(\frac{h}{R}\right) \quad (13)$$

when both particles have the same charge Q [38, 39]. Here ϵ_0 is the vacuum permittivity, h is the thickness of the oxide overlayer, and $g\left(\frac{h}{R}\right)$ is a function that only depends on geometry and that must be evaluated numerically. Similarly, when one particle has a charge Q and the other is uncharged, F_Q can be expressed as

$$F_Q = \frac{Q^2}{16\pi\epsilon_0 R^2} \times f\left(\frac{h}{R}\right) \quad (14)$$

where $f\left(\frac{h}{R}\right)$ is another geometry-dependent function that must be evaluated numerically. The sign of $g\left(\frac{h}{R}\right)$ is everywhere positive (i.e., the charged particles repel), whereas the sign of $f\left(\frac{h}{R}\right)$ is everywhere negative (i.e., the charged and uncharged particles attract). The absolute values of $f\left(\frac{h}{R}\right)$ and $g\left(\frac{h}{R}\right)$ are plotted against $\frac{h}{R}$ in Figure 9. For the Ti-6Al-4V powders characterized in this work, $\frac{h}{R} \sim 10^{-4}$ so Figure

9 shows that the force between a charged and an uncharged Ti-6Al-4V particle is greater than that between two charged particles. For this reason, we only use Eq (14) in what follows.

Combining Eqs 11 and 14 gives the following relationship for the maximum electrostatic force in the powder bed during preheating:

$$F_Q = \frac{\pi R^2}{16\epsilon_0} \left(J\eta\tau \left(\frac{1-e^{-\frac{\Delta t}{\tau}}}{1-e^{-\frac{T}{\tau}}} \right) \right)^2 f\left(\frac{h}{R}\right). \quad (15)$$

Figure 10 shows Eq 14 normalized and plotted as a function of $\tau/\Delta t$ for two values of $\frac{h}{R}$. It is noted that in Figure 8, the forces are all in-plane because the particles are all in-plane. This is not the case in a real powder bed, where the particles can have slightly different heights because of the surface roughness of their substrate. While this makes it more difficult to accurately calculate the direction of the largest force, the magnitude of the largest force can still be estimated using Eq 15.

6. Stability Criteria

Smoking would be unavoidable were it not for gravity, adhesion, and friction, which all serve to restrain the particles. Given the range of particle diameters used in e-beam additive manufacturing (40 to 130 μm), the largest of these stabilizing forces—by several orders of magnitude—is that due to gravity [40, 41]. Thus, if we assume that F_Q is pointed out of the powder bed, smoking should only occur when F_Q is much larger than the gravitational force, or

$$\rho g \frac{4}{3} \pi R^3 < \frac{\pi R^2}{16\epsilon_0} \left(J\eta\tau \left(\frac{1-e^{-\frac{kD}{v\tau}}}{1-e^{-\frac{T}{\tau}}} \right) \right)^2 f\left(\frac{h}{R}\right) \quad (16)$$

where g is the acceleration of gravity and ρ is the theoretical density of the feedstock material, and we have eliminated Δt using Eq 5. For Ti-6Al-4V particles, the left hand side of Eq 16 is on the order of 10 nN, which means the charge on these particles must be kept below 10^{-14} C. If we use as inputs to Eq 16 values representative of the Arcam e-beam additive manufacturing process ($R = 40 \mu\text{m}$, $J = 40 \text{ kA/m}^2$, $D = 1 \text{ mm}$, $v = 10 \text{ m/s}$, $T = 10^3 \text{ s}$, $\eta = 1$) and solve for τ , we find that τ must be less than 0.5 ns to avoid smoking during the pre-heating of Ti-6Al-4V powders.

Inspection of the right side of Eq 16 suggests a number of strategies for suppressing smoking, such as increasing the beam speed, decreasing the beam diameter, and decreasing the current density. Additionally, since $f\left(\frac{h}{R}\right)$ scales as $R^{0.88}$ over the typical range of $\frac{h}{R}$ values, Eq 16 indicates that the powder should become slightly more resistant to smoking with increasing particle size, which is consistent with our experience.

Finally Eq 16 has an exponential dependence on τ which means decreasing τ is an especially effective way to suppress smoking when either $\tau < D/v$ or $\tau > T$. As mentioned above, τ is the product of the resistivity and permittivity of the oxide overlayer [35], thus decreasing either of these properties will lower τ . In practice, modifying the resistivity of the overlayer is more straightforward than altering its permittivity. Approaches to decreasing the resistivity include adjusting the alloy chemistry so that the particles form more conductive oxide overlayers [8, 42], or tuning the processing so that the particles grow ultrathin overlayers through which electrons can tunnel [29, 30, 43-45]. As for the design of new parameter sets, most oxide overlayers are either ionic conductors or semiconductors with electrical resistivities that exhibit an Arrhenius law temperature-dependence [44-48]. For this reason, increasing the temperature of the build envelope can decrease the resistivity of the overlayer and make the powder more resistant to smoking. For example, we found while printing TiAl parts that the powder bed can sustain, without smoking, a current density at 1100 °C that is at least twice as large as the current density it can sustain at room temperature.

Practices that retard oxide growth, and prevent consequent increases in resistivity, should also help suppress smoking. These include storing the powders under vacuum and limiting the number of times a powder is reused [49]. Relatedly, the connection between τ and the resistivity of the oxide overlayer could be used for quality control. As an example, if a powder is being stored, periodic measurements of the resistivity of its overlayer could be used to check for increases in τ that would imply an increased susceptibility to smoking [50].

As a final point of discussion, we note that melting can precede, and therefore prevent smoking. Consider, for example, an experiment where a region of the powder bed is repeatedly scanned by an e-beam, and the current density of the e-beam is incremented after each pass, while the other process parameters, including the preheat temperature of the powder bed, are held fixed. In this experiment, the irradiated particles would remain undisturbed until the current density reaches some critical value, causing the particles to either melt or smoke. The particles would melt only if the critical current density associated with melting, J_{melt} , was less than that associated with smoking, J_{smoke} ; otherwise, they would smoke.

Following this argument, we can develop a melt-before-smoke criterion. J_{smoke} can be estimated using Eq 16, while J_{melt} can be calculated using the following relationship due to Ashby and Easterling [51]:

$$J_{\text{melt}} = \left[\frac{c\lambda\pi}{2} \left(\frac{T_m - T_0}{\eta} \right)^2 \frac{v}{v_{\text{acc}}^2 D} \right]^{1/2} \quad (17)$$

where V_{acc} is the accelerating voltage of the e-beam, λ is the thermal conductivity of the workpiece, c is the specific heat per unit volume of the workpiece, and T_m and T_0 are the melting and preheat temperatures of the workpiece. Though Eq 17 was originally developed for solid materials, it should also approximately describe incipient melting of the powder-bed in e-beam additive manufacturing. Eqs 16 and 17 can be combined to yield an inequality that, if satisfied, indicates the particles will melt before they smoke:

$$\frac{128}{3\pi} \frac{D\epsilon_0 R \rho g}{c\lambda v} \left(\frac{V_{\text{acc}}}{T_m - T_0} \right)^2 > f\left(\frac{h}{R}\right) \left(\tau \left(\frac{1 - e^{-\frac{kD}{v\tau}}}{1 - e^{-\frac{T}{\tau}}} \right) \right)^2. \quad (18)$$

According to Eq 18, increasing the accelerating voltage makes it more likely that melting will precede smoking; this is physically reasonable since changing V_{acc} affects the energy, but not the net charge, injected into the powder bed. In addition, from the above discussion, we know that the τ of Ti-6Al-4V powders must be less than 0.5 ns in order to suppress smoking during pre-heating. If we insert into Eq 18 this τ value, the standard melt parameters used when printing Ti-6Al-4V parts with the Arcam process ($D = 200 \mu\text{m}$, $v = 0.5 \text{ m/s}$, $T = 10^3 \text{ s}$, $T_0 = 900 \text{ K}$, $V_{\text{acc}} = 60 \text{ kV}$), and the physical properties of Ti-6Al-4V ($\rho = 4.43 \text{ g/cm}^3$, $\lambda = 6.7 \text{ W m}^{-1} \text{ K}^{-1}$, $c = 2.33 \text{ J cm}^{-3} \text{ K}^{-1}$), we find that Eq 18 is satisfied. This analysis therefore predicts that Ti-6Al-4V powder will not smoke during the melt operation if it does not smoke during pre-heating, consistent with experimental observations.

7. Conclusions

We have characterized the surface of two commercial Ti-6Al-4V powders using depth-profiling XPS, and have found an oxide overlayer on the particles that was several nm thick. Although this overlayer and the native oxide that forms on bulk Ti-6Al-4V under ambient conditions have similar compositions, the particle overlayer is significantly thicker. In light of our results, and those of other studies on the surface chemistry of atomized powders, it appears that atomized powders (and even some hydride-dehydride powders) have a thick oxide scale, which can electrically insulate the particles and cause charging during e-beam additive manufacturing.

Powder bed charging can be modelled by approximating the e-beam as a current source and the particles as capacitors where the overlayer is the dielectric. The model developed in this paper demonstrates that during the melt operation, the dimensionless group $v\tau/D$, which is the ratio of the charge dissipation time constant to the beam interaction time, determines both the shape of the charged region and the maximum charge on the particles. The model also shows that there are three different regimes of charging behaviors during the pre-heat operation, and that the regime active under a given set of conditions depends on the

relative magnitudes of the timescales associated with charge dissipation, beam-particle interactions, and beam rastering.

The model's predictions of powder bed charging are used to develop two design criteria. The first criterion predicts operating conditions under which the powder bed will smoke (with obvious application in process design). This criterion indicates that higher powder bed temperatures, larger particle sizes, and higher beam speeds should generally help suppress smoking; all of these trends are consistent with what is observed in practice. The second criterion predicts when particle melting will intervene and prevent smoking. Importantly, this criterion indicates that smoking should occur more frequently during pre-heating than during melting, in line with our observations.

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Table 1: Nominal compositions listed in at% of the gas-atomized and hydride-dehydride powders. The powder suppliers, Reading Alloys and TLS GmbH & Co., provided these values.

Figure 1: Photoelectron spectra from as-received and sputter-etched Ti-6Al-4V powders.

Table 2: Compositions listed in at% of the as-received and sputter-etched surfaces as measured by XPS.

Figure 2: Core level photoelectron spectra for Ti, Al, V, C, and O. Data from the as-received and sputter-etched surfaces are shown.

Figure 3: Schematic of the build envelope in cross-section showing the loose powder particles, solid material, and partially sintered material.

Figure 4: Schematic of the powder particle-substrate system and the equivalent circuit. The e-beam acts as a current source while the particle, the oxide overlayer, and the substrate act as a capacitor where the overlayer is the dielectric. Note that because the mean penetration depth of the electrons is roughly three orders of magnitude larger than the oxide thickness, most of the electrons that strike a particle will pass through the oxide and come to rest in the metallic core.

Figure 5: Steady-state charge distribution in a row of irradiated particles. The shaded region indicates the instantaneous position of the beam. The values of $V\tau/D$ used to calculate each charge distribution are indicated.

Figure 6: Particle charging profile during pre-heating, assuming $\tau/T = 2$. The curve exhibits an initial transient that lasts several τ , after which it settles into a cyclic stationary state.

Figure 7: Maximum charge on a particle during the preheat operation as function of the ratio $\tau/\Delta t$, assuming $T/\Delta t = 10^3$. The curve can be divided into the three regions indicated.

Figure 8: Charge distribution in a close-packed monolayer of monodisperse powder particles irradiated by a circular, top-hat beam. The color of the particles corresponds to their normalized net charge. The arrows indicate the directions and relative magnitudes of the electrostatic forces acting on the particles. The instantaneous position of the beam is indicated by the dashed circle.

Figure 9: Absolute value of $f(h/R)$ and $g(h/R)$ as a function of h/R .

Figure 10: F_Q as a function of $\tau/\Delta t$ assuming $T/\Delta t = 10^3$. The values of h/R used to calculate each curve are indicated.

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Table 1

synthesis method	Ti	Al	V	O	C
gas-atomization	85.9	10.2	3.5	0.33	0.04
hydride-dehydride	85.2	10.6	3.6	0.36	0.15

Table 2

	Synthesis method	Ti	Al	V	O	C
as-received	gas-atomization	16.3	9.6	0.9	53.0	19.9
	hydride-dehydride	20.0	2.5	1.0	52.3	23.7
sputtered	gas-atomization	41.4	7.6	1.3	30.0	19.3
	hydride-dehydride	42.9	4.9	2.1	32.3	17.5