Equalization of Metal Powder for Binder Jet Printing

Michelle Niu, Krzysztof Nauka

HP Inc, 1501 Page Mill Rd., Palo Alto, CA 94304

Abstract

Metal powders used in additive manufacturing often face the issue of variable powder surface characteristics, causing inconsistent part quality. As such, a "homogenization" treatment for metal powder surfaces may be advantageous for relevant fabrication processes. By using high-powered xenon flash lamp to rapidly heat powder samples, the surface energy of the powder particles was brought to the same value regardless of the powder source and past usage. Pulse-heating the powder caused the atomic structure of particle surfaces to undergo rearrangement and removed adsorbed moieties. Effects of this treatment on metal powders have been investigated and evaluated by measuring the time before water droplets are absorbed on treated and untreated thin layers.
Keywords: metal powder surface energy modification, additive manufacturing, high energy light irradiation

Introduction

Industrial processes involving metal part fabrication uses metal powders of a various range of particle size distributions, up to several hundred microns, such as injection molding where particles are compacted and subjected to heat treatments or additive manufacturing where the particles are spread into thin layers and selectively bonded in an iterative process. Regardless of process, the particles' surface properties, which can be summarily described as the powder surface energy, can impact the resulting part quality by affecting the optimal packing density or powder spreadability.

Powder surface energy is influenced by several factors: particle size, morphology and structural defects, and surface atomic arrangement. Micro-crystallographic structure within a particle can also impact surface energy [1, 2]. In addition, as powders are often kept in storage for extended periods, interactions between the particles and the atmospheric environment as well as physiosorbed or chemisorbed impurities can alter the powder surface energy between manufacture and use [3, 4]. Some of these impurities may have a negligible or even positive affect on part quality, but often these impurities have a negative impact [5]. In additive manufacturing, powder recycling can accumulate additional residual impurities from the process; repeated recycling, while economical, can have cumulative detriment to powder characteristics and part quality.

One avenue to consistent part quality is to ensure comparable or ideally, identical, powder surface energy, regardless of powder source and use. Consequently, there has been a great body of work focusing on thermal powder conditioning via prolonged bakes prior to use [6]. However, most of the work thus far are powder and application specific. In this paper, we focus on a more versatile "equilibration" technique independent of metal, source, and application, as well as a demonstration of a fast powder surface evaluation methodology.

Experimental Procedure

A range of metal powders were used in this work, although the primary focus was on gas atomized spherical powders with known size distributions. In some cases, the powder, as a result
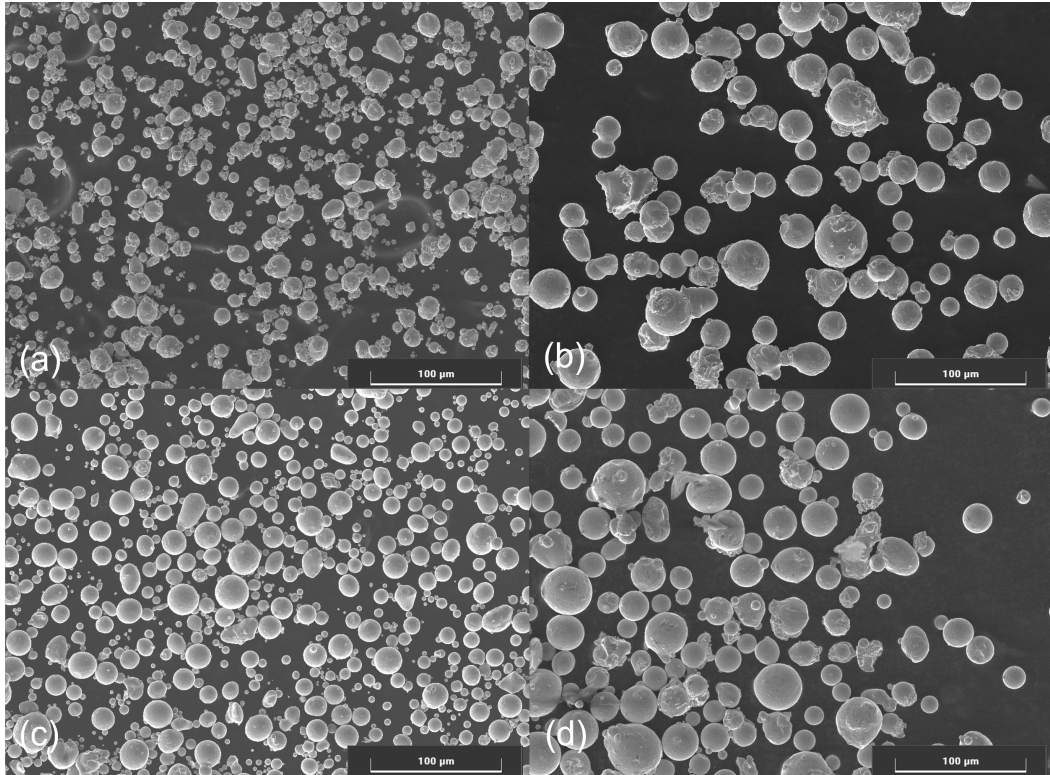
Figure 1: SEM Images of some powders examined: (a) copper, (b) Hastelloy, (c) stainless steel 316L, and (d) Inconel.

Powder	Composition	Particle size D50 (µm)
SS1	Stainless steel 316L	17
SS2	Stainless steel 316L	21
SS3	Stainless steel 316L	34
SS4	Stainless steel 316L	32
SS5	Stainless steel 17-4PH	32
Ti1	Ti-6Al-4V	38
Ti2	Ti-6Al-4V	36
Ti3	Ti	27
Mo	Mo	38
Al	AlSi12	46
Inconel	Inconel 718	32
Hastelloy	Hastelloy C762	32
Cu1	Cu; atomization process A	14
Cu2	Cu; atomization process B	14
FeNiCoMo	Fe:Ni:Co:Mo (68:16:8.5:4.5, Ti balance)	33

Table 1: Subset of commercial powders used in the experiment and their D50 particle sizes. Details of additives and contaminants are not available.

of the atomization process or electrostatic forces, has small particle agglomerates on the main particles, as seen in Figure 1a and 1d. Adding chemical agents can reduce the electrostatic forces and may be present in some of the samples [7, 8]. Table 1 lists the samples used along with their D50 powder size.

A Novacentrix PulseForge 1300, a commercial Xe flash system, was selected as the energy source for this experiment because of its ability to deliver rapid, high-energy optical pulses with a broadband spectrum spanning from 250-1000 nm. The particles' surface energy can be altered by exposure to high temperatures to remove impurities or modify surface atomic arrangement. However, it is important to avoid excessive temperatures to prevent powder sintering or melting. Consequently, maintaining the particle structural integrity while altering its surface energy requires an instantaneous rise in surface temperature between 40-80% of bulk metal melting point while the interior temperature remains low [9]. This can be achieved with short, high-energy pulses the Xe flash lamp provides and finite heat transfer velocity particularly when irradiating a thin layer of powder. This was confirmed by IR imaging where samples subjected to the most extreme parameters showed rapid dropping of surface temperature within 0.5 s of pulse termination did not exceed 110°C, even after repeated pulsing.

The energy dose delivered per 20 ms pulse was varied between 5-50 J/cm^2. Considering that the pulse has a rise time of 0.5-1 ms and a fall time of 1-2 ms, the total steady-state duration ends up 7.5-15% shorter than the programmed 20 ms. The baseline number of flashes samples were subjected to was 5 flashes; however, effects of fewer flashes on powder treatment were also investigated. Delay between pulses ranged from 0.8-4 s depending on the pulse energy and is a limitation of the system recharge speed. Three to five samples were measured for each experimental parameter.

The PulseForge 1300 is equipped to accommodate different atmospheric environments. As such, both an inert (Ar) and reductive (Ar-H$_2$) environment were explored at atmospheric pressure. Samples were not irradiated when exposed to air ambient in order to prevent sample oxidation. The lack of oxide formation was visually confirmed via lack of surface discoloration and with EDX. Both ambient and heated samples were investigated, the latter taken up to 100°C with the built-in resistive heater.

Metal powders were mechanically spread into thin layers between 70-800 μm on a glass substrate, then placed into the PulseForge system where a rough pump-purge sequence, down to sub-10 millitorr, is initiated before filling with the desired atmosphere and irradiated. To determine the effects the irradiation had on the powder surface energy, the samples were removed from the Xe flash system and evaluated with a Krüss Drop Shape Analyzer (DSA100) within 30 min of treatment [10]. A 4 μL water droplet is automatically deposited by the DSA100 onto the surface and its change in contact angle over time monitored with the DSA100's camera system. Because the water surface tension is a constant between samples, the length of time for a droplet to be absorbed is a proxy for the powder surface energy, referred to as the "droplet residence time". Although this is a qualitative approximation technique, the droplet residence time is sufficient to demonstrate powder surface energy changes as a function of Xe pulse irradiation. Water was selected for its high surface tension to facilitate the evaluation of high and low surface energy powders.

Results

The results of the powder-water interaction can be categorized into three cases, as shown in Figure 2 below. First, when the powder surface energy is comparable to that of water's surface tension, the droplet residence time is low, typically <0.5 s, showing that the droplet is quickly absorbed (Fig. 2a). In contrast, when the powder surface energy is much lower than water surface tension, the converse is true: the droplet residence time is high, exceeding tens of seconds, and the droplet remains unchanged on the surface (Fig. 2b). In the third case, the droplet disrupted the powder surface upon contact. This phenomenon is likely due to shallow penetration of irradiation, resulting in a thin layer of treated powder with high surface energy (HSE) over the remaining untreated, low surface energy (LSE) powder. As the droplet wets the top HSE region and reaches the interface between the two contrasting surface energies, the interaction with the LSE powder deforms the surface (Fig. 2c).
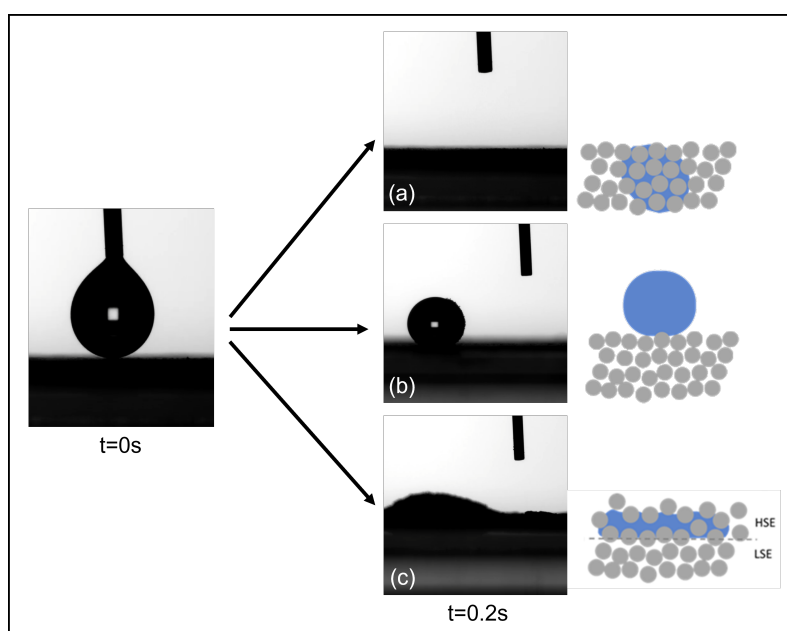

Figure 2: Video stills and schematics illustrating the categories of droplet behaviors 0.2 s after droplet deposition showing the case of (a) high surface energy where the water droplet is quickly absorbed into the powder layer, (b) low surface energy where the water droplet remains on the surface for an extended period, and (c) both high and low surface energy within the sample layer, causing surface disruption when the water droplet reaches the interface.

Ray tracing calculations showed that the pulse irradiation can reach 80-170 µm below the surface before full absorption. The absorption depth is dependent on variables like the metal, reflectivity, particle size, morphology, and packing density. Additionally, heat transfer from convection and conduction between particles may increase the depth of heated particles to 100-250 µm. These calculations were confirmed by monitoring the depth of partial fusion of samples exposed to increased flash energies and further evidenced by samples that fall under the third category.

Prior to irradiation, the powders used has a wide range of initial surface energies; some already have short droplet residence times while most have severe surface energy mismatch with

water. The following experimental parameters were initially held constant: the flash envelope conditions (20 ms), sample atmosphere (inert; Ar), powder temperature (100°C), and the number of pulses (5x). Energy density per pulse was varied from 9-20 J/cm^2. Figure 3 below shows the direct correlation between the energy density and droplet residence time. There is a clear indicator of a required threshold energy for the powder surface energy to change; this threshold energy is material dependent. At higher energy densities, the residence times are comparable across powders, indicating it is feasible to achieve similar final surface energies despite their initial states.
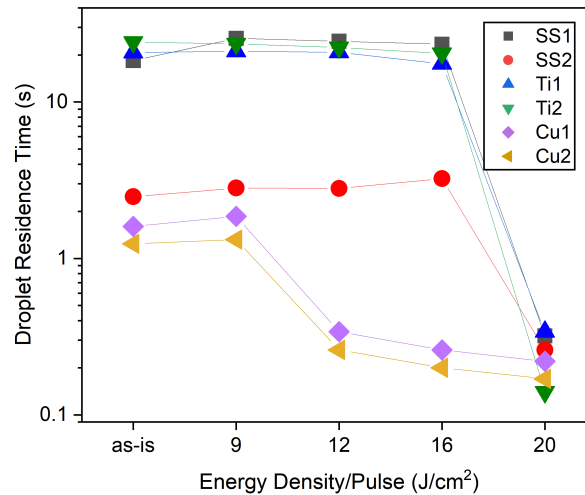

Figure 3: Droplet residence time as a function of energy density/pulse for a subset of treated powders. As-is refers to the powder without any flash treating.

Considering the energy cost and efficiency, the powder temperature and number of flashes were reduced to see if equilibration of powder surface energies still occurred. Pulse energy density was held constant at 20 J/cm^2 because of its consistent effect on surface energy independent of material, as were the other variables. Decreasing the powder temperature from 100°C to ambient (~ 25°C) had largely minimal effects, as long as the threshold energy was met. Figure 4a shows that at low energy conditions (1x; RT), droplet residence times and droplet behaviors degrade. Reduction of flashes from 5x to 3x and 1x saw minimal changes, though the sensitivity to flash reduction was also material dependent (Fig. 4b). Further tuning of flash parameters may yield optimized results balancing efficiency and cost.

As foreign impurities are a likely contributor to initial low surface energies, a reductive environment with the same initial experimental parameters (100°C, 5x flash) was briefly explored to see if the forming gas could further react with impurities and improve results. However, changes to the experimental atmosphere had no perceivable difference in results. It is possible that the changes are difficult to capture with this qualitative methodology due to the complexity of metal particle surfaces and impurities interactions. In addition, it is possible that the impact of atmospheric changes is metal-dependent.
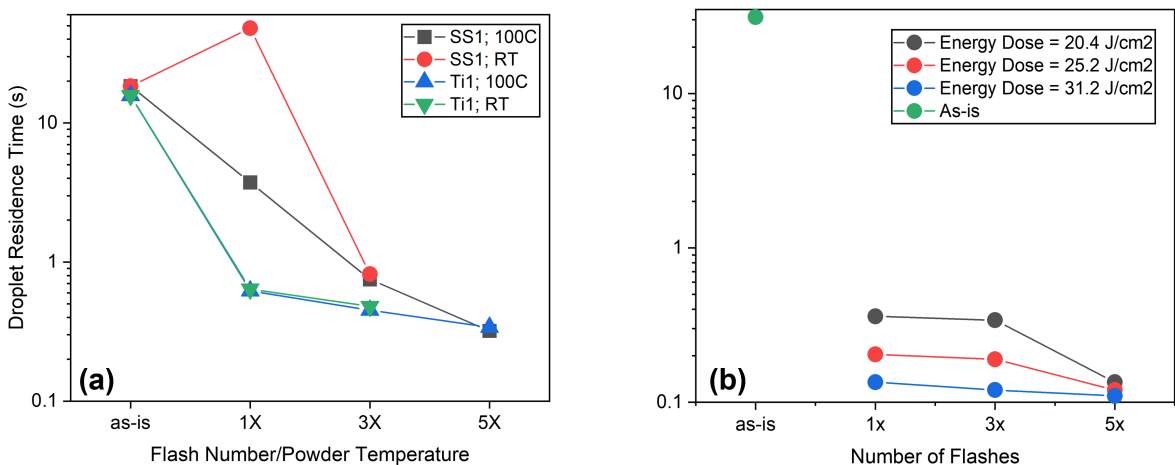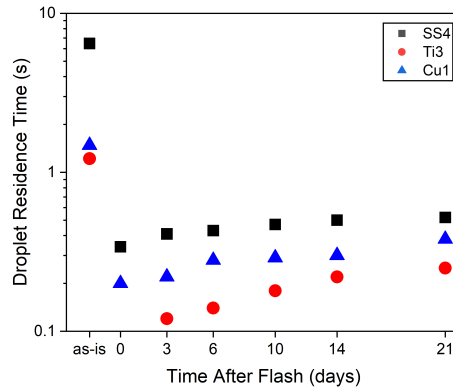
Figure 4: (a) Droplet residence times increase as the total energy decreases. Broadly speaking, the treated powders still outperformed nontreated powders, but a threshold energy is evident for consistent results. (b) For the same material (stainless steel), the number of flashes imparted on the sample has negligible effect on droplet residence time.

To further investigate the effect of impurities on metal powders, the specific case of carbon contamination in titanium alloys was chosen because of its use case in additive manufacturing [11, 12]. Impurities like carbon, especially as residue from binder jet agents, pose a challenge for titanium additive manufacturing due to its impact on mechanical properties. Two titanium alloys, one being a virgin, high-performing powder for printing (Ti-1) and one having a known carbon contamination due to recycling (Ti-2), were both flash treated and demonstrated an increase in surface energy (Fig. 3). Furthermore, Ti-2 was intentionally doped with additional carbon using 0.01 wt% sodium dodecyl sulfate and then irradiated. Chemical compositions of all samples were analyzed with elemental combustion technique (LECO) and showed reduction of carbon content after Xe treatment, tabulated in Table 2. While this can only remove some surface contaminates, repeated flashing may further reduce the carbon content.

Sample	Carbon wt% (LECO)
Ti1 – as-is	0.008
Ti1 – flashed once	0.007
Ti2 – as-is	0.016
Ti2 – flashed once	0.013
Ti2 – flashed three times	0.010
Ti2 – intentionally contaminated	0.038
Ti2 – intentionally contaminated and flashed 3X	0.027

Table 2: Combustion analysis (LECO) results of virgin, recycled, and carbon-doped titanium powders before (as-is) and after flash treatment.

Aside from removing absorbed moieties, increasing powder surface temperatures to 50-70°C of the bulk melting point can trigger rearrangement of surface atomic crystalline structures to a more thermodynamic configuration [13]. Because the rearrangement occurs at high temperatures, over time, the effects of the flash treatment may deteriorate as the surface atoms spontaneously reconfigure to thermodynamic equilibrium under ambient conditions. Selected treated powders stored in lab ambient conditions were periodically measured over the course of a few weeks. Figure 5 on the right shows the gradual decrease in surface energy of the powders. Rate of surface energy change is likely dependent on the initial powder conditions, metal type, and flash parameters.

Figure 5: Droplet residence time as a function of aging samples under ambient conditions show the time-sensitivity of the flash treatment.

Conclusion

We have demonstrated with a high powered Xe flash lamp the feasibility of increasing the surface energy of a thin metal powder layer to a consistent level regardless of the metal used and powder history. The changes in surface energy are likely due to rearrangement of atomic structure of particle crystalline surfaces and removal or adsorbed impurities. Critically, the samples did not sinter or melt during the treatment, due to the localized nature of the short pulse durations and finite heat propagation velocity within the particle, thus ensuring that only the exposed particle surfaces and not the interiors were heated. This method can be implemented in an iterative process where untreated powder can be spread onto a treated layer for processing until enough material has been processed. The iterative layer-by-layer nature of this technique is highly compatible with that of binder jet printing and can be easily implemented where each powder layer is irradiated in the 3D printer before printing.

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Supplemental Material

In addition to commonly used metals (stainless steel, titanium, and copper), a wide variety of other metals, both ferrous and non-ferrous, were investigated. In the figure below, it is clear that all materials treated demonstrate the same trend of reduced droplet residence time as energy density increases and that there is a clear material dependence on threshold energy for effective treatment. The samples were subjected to the following flash parameters held constant while varying energy density: inert atmosphere (Ar), initial powder temperature of 100°C, and five flashes.
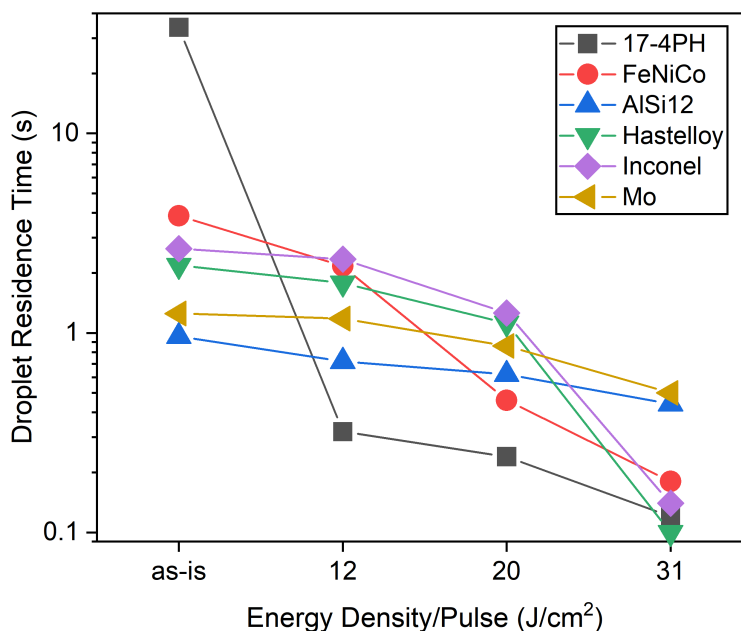

Figure 6: Xe flash heating results of several other metal powders.

Two samples of stainless steel 316L and titanium powders (below) were further examined regarding the effects of powder temperature during flash heating and the number of flashes. Again, while the exact energy required for effective change in droplet residence time varied by material, once the threshold energy is reached, the initial powder temperature and the number of flashes do not affect the droplet residence time. For example, powder temperature is seen to have a larger effect on the two stainless steel powders compared to the titanium powders before the threshold energy is reached.
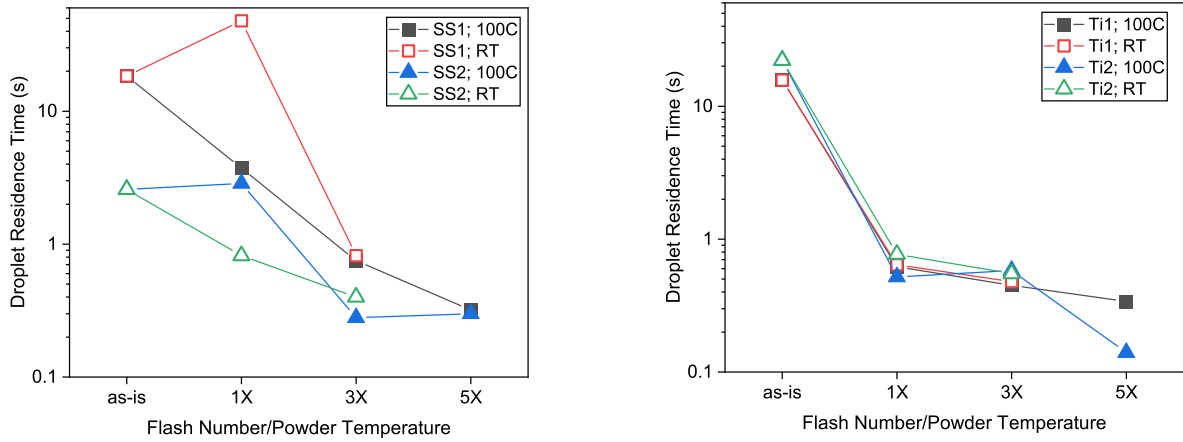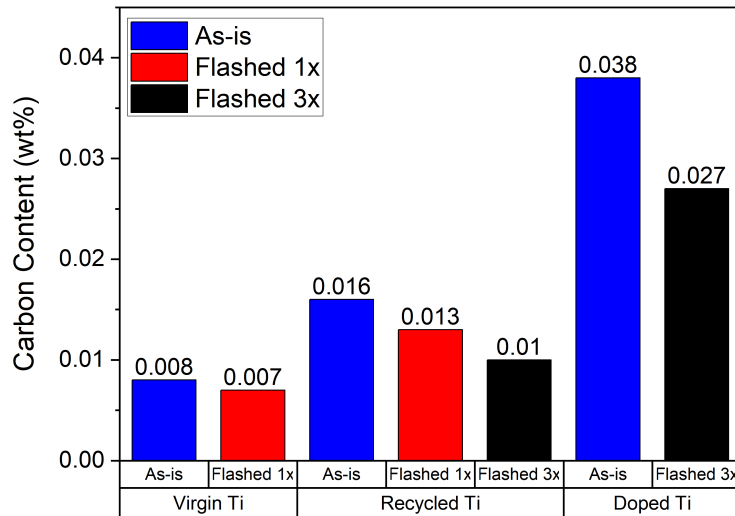
Figure 7: Energy density was held constant at 20 J/cm^2 for all samples shown. Left: Droplet residence time dependence on initial powder temperature (room temperature or 100°C) for stainless steel 316L. Right: Droplet residence time dependence on powder temperature for titanium.

The figure above is a graphical representation of Table 2. As the powder is flash heated, the carbon contaminant content decreases, regardless of powder origin.