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White paper

Investigating the effects of multiple re-use of Ti6Al4V powder in additive manufacturing (AM)

Abstract

Metal powder re-use in additive manufacturing (AM) has been investigated using a Renishaw AM250 system and titanium alloy Ti6Al4V ELI (extra low interstitial) powder. The study is a follow-on from the encouraging results obtained in a previous study in which the chemical and physical effects of re-using metal powder through the AM250 twenty times was investigated. In order to increase the robustness of the study, more tensile bars were built for each run; three to be tested with an 'as built' surface and three machined. Powder capture capsules and density blocks were also built.

A single batch of powder was cycled through Renishaw's additive manufacturing process for a total of 38 builds until there was no longer enough powder remaining for a test sample height. Powder was analysed for oxygen and nitrogen content, Hall flow, particle size distribution (PSD) and density. There was found to be a small but steady increase of both oxygen and nitrogen concentrations in the powder as the build number increased. At around 16 builds the oxygen level started to fluctuate around the upper limit for the specification. Nitrogen stayed within the material specification maximum limit as well as the more stringent lower allowable 300 ppm stated for some other grades. It is likely that under normal running conditions with regular topping up of the silo with virgin powder these levels will remain within the boundaries of the ELI specification. Both levels stayed well within the boundaries of the grade 5 specification. PSD values shifted very slightly upwards due to gradual loss of smaller particles resulting in an increase in Hall flow speed. Upper tensile strength was found to be higher for the machined, compared to the rougher 'as built' tensile bars. Overall it was concluded that the changes in the powder over the period of the study are not significant enough to affect the material parameter settings, and there is no evidence to suggest powder disposal will be necessary.

Introduction

Renishaw additive manufacturing systems use metal powder bed fusion to build complex components directly from CAD data. Objects are built layer-by-layer by spreading out fine metal powders and selectively melting areas with a high-power laser. Any un-melted powder remaining after a component has been built can then be re-used for another build. There is a question mark over whether there is a limited number of times that metal powders can be cycled around an AM process because chemical and physical properties are bound be changed, but to what extent?

There are multiple factors which contribute to consistent, repeatable, and reliable AM builds, such as laser focus, filter condition, and z-axis movement – for this study we looked at feedstock (metal powder). The properties of the powder and the machine parameters that are used to process it are closely related, so the chemical and physical properties of the powder are critical. Manufacturers are naturally concerned that the condition of the powder they are processing is predictable and stable in order to have confidence in the quality of the manufactured components.

Economics is also an issue; the fine metal powder used in laser melting can be costly, so waste should be avoided. In most cases, only a small proportion of the powder that is laid down in a build process is actually melted into a component - most is left un-melted and is therefore available for re-use.

Some of the benefits of near-net-shape manufacturing depend on such recycling. If we are forced to consider un-melted powder as contaminated and therefore unfit for re-use, then the cost of additive manufactured parts is likely to be prohibitive for many industries.

How can the powder be affected by the AM process?

Both chemical and physical properties of the powder can potentially be affected by the AM process, however this will most likely differ depending on the material type.

Renishaw AM systems use an inert argon atmosphere which is generated by first creating a vacuum and back filling with the inert gas. Builds generally start at low oxygen content of < 1000 ppm, with the possibility of a starting atmosphere of < 100 ppm if required. The oxygen content in the chamber drops to approximately < 10 ppm after the first few layers. For this study all builds began at < 1000 ppm oxygen content. For titanium powder it is important to have a low oxygen (and nitrogen) atmosphere due to the material's propensity to absorb these gases as bulk impurities: residual heat from the weld pool can cause heated particles to take up oxygen or nitrogen forming oxides and nitrides. Within the build chamber this effect is minimal due to the inert argon atmosphere, however if re-used many times, will the cumulative effect cause the powders to become out of specification?

Physically the powder can be affected in a variety of ways, and again the majority of these effects will be due to powder particles being either near the weld pool or as a result of being ejected from the weld pool.

Physical properties of metal powder that will have an effect on the way it behaves within the AM system include:

- Shape; a spherical morphology is preferable compared to angular or spongy
- Packing/density
- Particle size distribution (PSD)
- Flow

Flow of the powder is very important when dosing from the silo and for creating consistent layers across the bed – this is directly affected by shape, density/packing and PSD. If the PSD is too wide or bimodal the smaller particles will sit in the spaces between the larger particles increasing packing and inhibiting flow. If the PSD is too narrow this could lead to insufficient packing and pores in the melted part (Figure 1.). Powder flow was measured using the Hall flow method (ASTM B213-13), it is a simple test in which the time taken for 50 g of powder to travel through a calibrated funnel is measured, giving a value with the units sg^{-1}. If the powder requires more than one tap or does not flow through the funnel the powder is determined as non-flowing.

Ejected particles may be misshaped due to partial melting; powder grains near the edge of the weld pool may become fused together but not attached to the part, creating irregular shaped agglomerates and 'satellites'. Oversized particles, and agglomerates will be sieved out after every build; this helps to control the PSD of the bulk.

Why titanium?

This study focuses solely on the recycling of titanium alloy, Ti6Al4V powder. Ti6Al4V alloy comprises of 90% titanium, 6% aluminium, 4% vanadium with low allowable levels of other elements including oxygen, nitrogen and iron.

Titanium alloys have a very high strength to weight ratio, they are approximately the same strength as steel but are only 45% of the mass. With high corrosion resistance and biocompatibility these materials are highly desirable for a range of applications. The fact that titanium is relatively expensive to buy and costly to machine explains why the material is not more widely used in manufacturing.

Buy-to-fly-ratio:

The term 'buy-to-fly ratio' is a term used in the aerospace industry to represent the amount of material required to produce a final component. For example, a 20 kg billet may be required to produce a 1 kg component with 19 kg of waste; a buy-to-fly ratio of 20:1. Ratios as high as this are common in aerospace, making the overall cost of a component very high – especially when considering expensive titanium. Additive manufacturing produces near net shape components meaning that buy-to-fly ratio values are closer to 1:1 with the majority of the waste produced from support material and any surface machining.

Further material savings can be achieved by re-designing the component to remove any sections of material not required for the function of the part.

Titanium alloy Ti6Al4V specification

Titanium and its alloys are known as 'getter' materials because when they are heated, for example when being heat treated or machined, they will absorb molecules from the air. In the case of titanium, oxygen and nitrogen will react to form oxides and nitrides inside the bulk and are referred to as interstitial impurities as they sit in-between the crystal lattice. Maximum allowable levels for these (and other interstitial impurities hydrogen (H) and carbon (C)) elements are stated in the grade specification for titanium and its alloys. If the levels become too high, the desirable material properties can be lost. Therefore

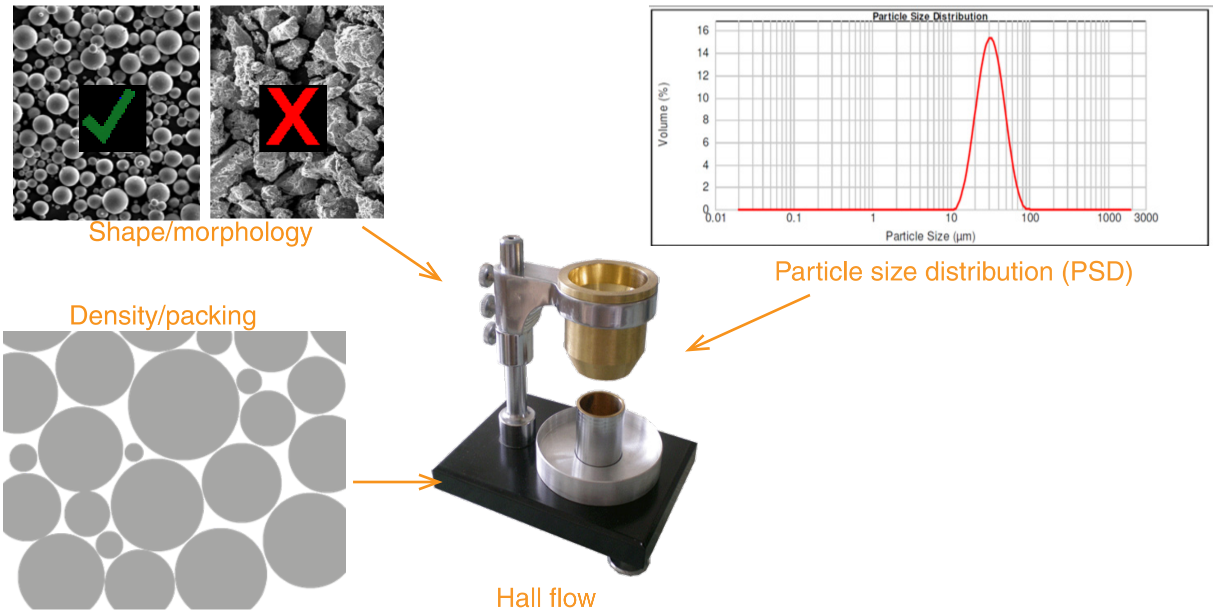

Figure 1. *Important physical properties of metal powders for additive manufacturing include shape/morphology, particle size distribution (PSD), density/packing and flow*

Element type	Element	Ti6Al4V grade maximum / %	
		Grade 5	Grade 23 (ELI)
Interstitial	Oxygen (O)	0.20	0.13
	Nitrogen (N)	0.05	0.05*
	Carbon (C)	0.08	0.08
	Hydrogen (H)	0.0125	0.0125
Alloying	Aluminium (Al)	5.5-6.75	5.5-6.5
	Vanadium (V)	3.5-4.5	3.5-4.5

* Some specifications state 0.03 %

Table 1. *Ti6Al4V grade specifications for interstitial and alloying elements*

it is highly important for titanium to be processed in an inert argon atmosphere to prevent it drifting out of specification.

Ti6Al4V is specified in two main grades- 23 otherwise known as ELI or extra low interstitial, and 5. Maximum allowable levels of some elements are highlighted in Table 1. These two grades are essentially the same, other than the maximum allowable levels of oxygen, and for some specifications, nitrogen. Renishaw uses ASTM 3001 13 ELI titanium alloy.

AM250 specification and powder handling

Table 2. shows some of the technical specifications of the AM250 used for this study.

The powder silo is located at the top of the machine. Advantages of this are that sieved powder from a previous build can be placed directly on top of the remaining powder in the silo. It can also be topped up during a build with virgin or used powder, however for this study only used powder was added.

The way that the argon atmosphere is generated is unique to Renishaw systems. First a vacuum is created in the chamber to remove any air and moisture. The chamber is then backfilled with argon creating an inert atmosphere for the build with < 1000 ppm O_2. This process takes approximately 10 minutes and requires 600 L of argon.

After the build, all un-melted material is directed into overflow bottles using the integrated glove box located in the door of the build chamber. Overflow bottles are then sealed ready for removal from the system. Once un-melted material has been removed from the build volume, the build chamber door is opened and the build plate removed.

Overflow bottles filled with un-melted powder from the build are directly connected to the sieve, which is kept under an inert argon atmosphere. An argon-filled overflow bottle catches the powder as it is sieved and is then used to replace the powder directly back into the silo.

All processes in place are there to ensure the integrity of the powder and safety of the user.

Experimental procedure

To fully understand the effects of re-using powder through the AM process using Renishaw systems the following formed the basis of the study:

- Use titanium as it is the most likely to pick up contamination from the air.
- Start with a single batch of virgin powder to fill the silo, and use the same AM250 system throughout.
- Carry out routine builds re-using the powder until there is not enough left to build full test sample height.
- Do not add any virgin or other powder to the batch at any point.
- Build standard test samples to analyse both powder and tensile properties over the period of re-use.
- Sieve un-melted powder to remove oversized material from each build before replacing into the silo.

In total, 38 AM builds were carried out over a period of 3 months.

Figure 2. *Renishaw AM250 systems at the Stone, Staffordshire, UK facility*

Build volume	250 mm × 250 mm × 300 mm
Build rate	5 cm^3/hr to 20 cm^3/hr
Layer thickness	20 µm to 100 µm
Laser beam diameter	70 µm at powder surface
Laser power	200 W
Power supply	230 V 1 PH 16 A
Power consumption	1.6 kWh
Gas consumption	< 30 L/hr

Table 2. *AM250 system specification*

For the majority of the builds the following test samples were built, a build example is shown in Figure 3.

- Capsule to capture approximately 60 g of powder.
- 3 x tensile bars to be tested as built
- 3 x tensile bars with +1 mm diameter for as machined testing
- Density block

This is an extreme analysis of powder re-use. Usually the silo would be topped up regularly with virgin powder, essentially refreshing the used powder; this study looks at the most extreme case of never refreshing the used powder.

What stages contribute to a re-use cycle?

After the silo had been filled with virgin metal powder the following stages illustrated in Figure 4. contributed to a re-use cycle:

1. AM build
2. Remove build plate
3. Sieve un-melted powder under argon
4. Replace sieved powder into the silo located at the top of the machine
5. Repeat cycle

Results

Composition

Figure 5. shows the oxygen content results from both studies. Compared to the first study the oxygen levels from the second study are generally higher, however the oxygen pick up rate is similar.

A few of the builds creep out of the ELI maximum range; builds 15, 25, 26, 27 and 33, all others are within the boundary of grade 23 ELI, and well within the grade 5 boundary.

Results from the first study showed all of the powder was within ELI limits for oxygen over 20 builds.

Nitrogen levels (Figure 6.) also showed a gradual increase, staying well within the 500 ppm maximum specification and coming above the 300 ppm maximum specification within the last few builds.

Under normal build conditions the silo is refreshed with virgin or unused powder once the level in the silo begins to deplete.

Figure 3. *An example of a build setup with 1. powder capture capsule, 2. tensile bars (×6) and 3. density block*

Addition of new powder should damp down the increase rate for oxygen and nitrogen, essentially keeping the levels steady and below the maximum allowable boundaries.

Melted parts require analysis for true effect. This analysis has not been carried out for this study. However, for reference, a 2015 paper titled 'Effect of powder re-use times on additive manufacturing of Ti-6Al-4V by selective electron beam melting' by Ma Qain *et al* finds that the tensile test bars analysed showed virtually identical levels to the powder analysed for the equivalent build.

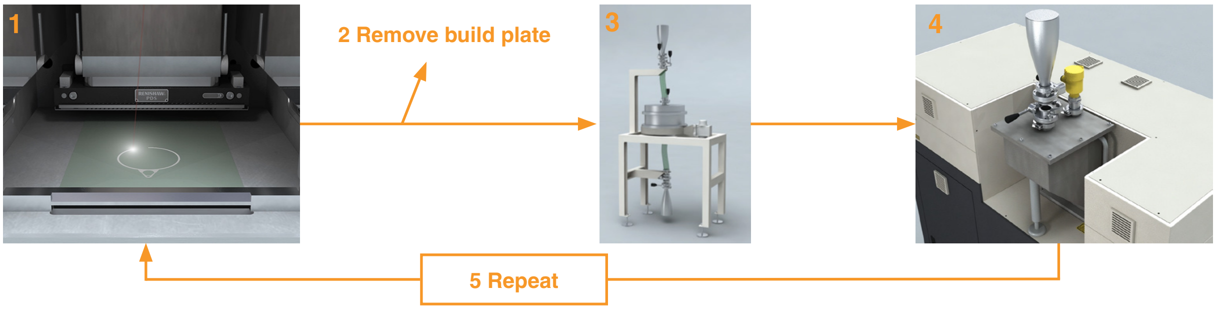

Figure 4. *A re-use cycle 1. Build, 2. Remove build plate, 3. Sieve un-melted powder, 4. Replace sieved powder into silo at the top of the machine.*

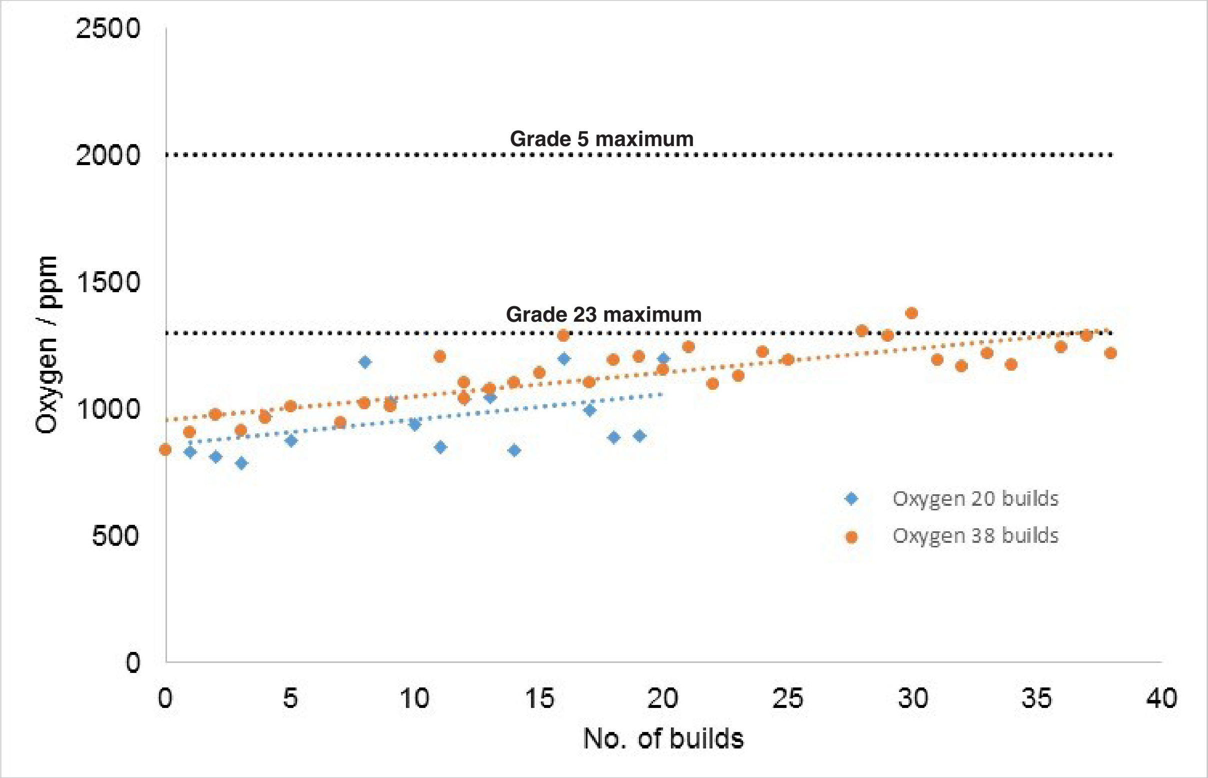

Figure 5. *Oxygen analysis over two separate re-use studies shows a gradual increase in concentration*

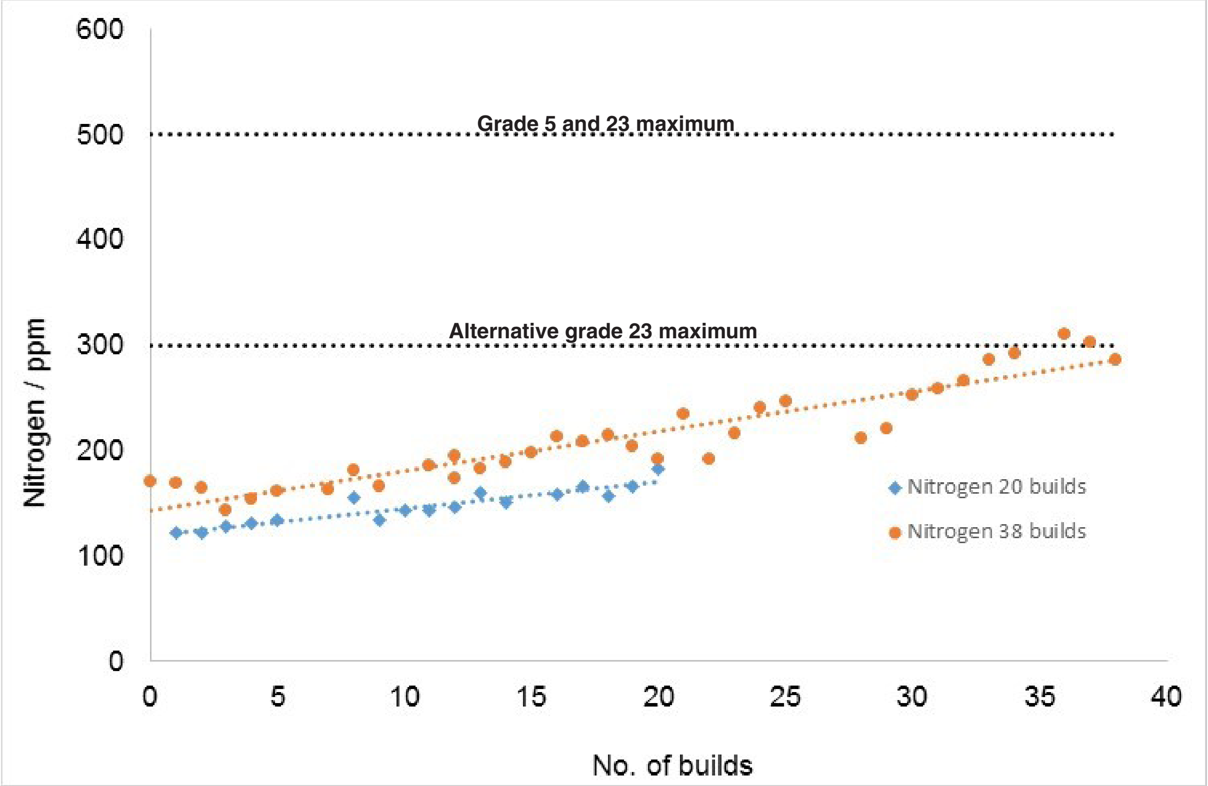

Figure 6. *Nitrogen analysis over two separate re-use studies shows a general increase in concentration*

Physical analysis

Particle size distribution (PSD) and flow

PSD was measured using a wet laser diffraction method. The D10, D50 and D90 values attained from the method represent the particle size in which 10%, 50% and 90% of the particles are equal to, or smaller than respectively.

Very little change was observed in the particle size distribution of the powder (Figure 7.). The differences between the 1st virgin and 38th build powder sample was most significant in the D10 value, a change of +1.30 µm – a very small difference. D50 and D90 values increased by +1.0 µm + 0.4 µm respectively.

There is a general tightening in the PSD over the re-use cycles

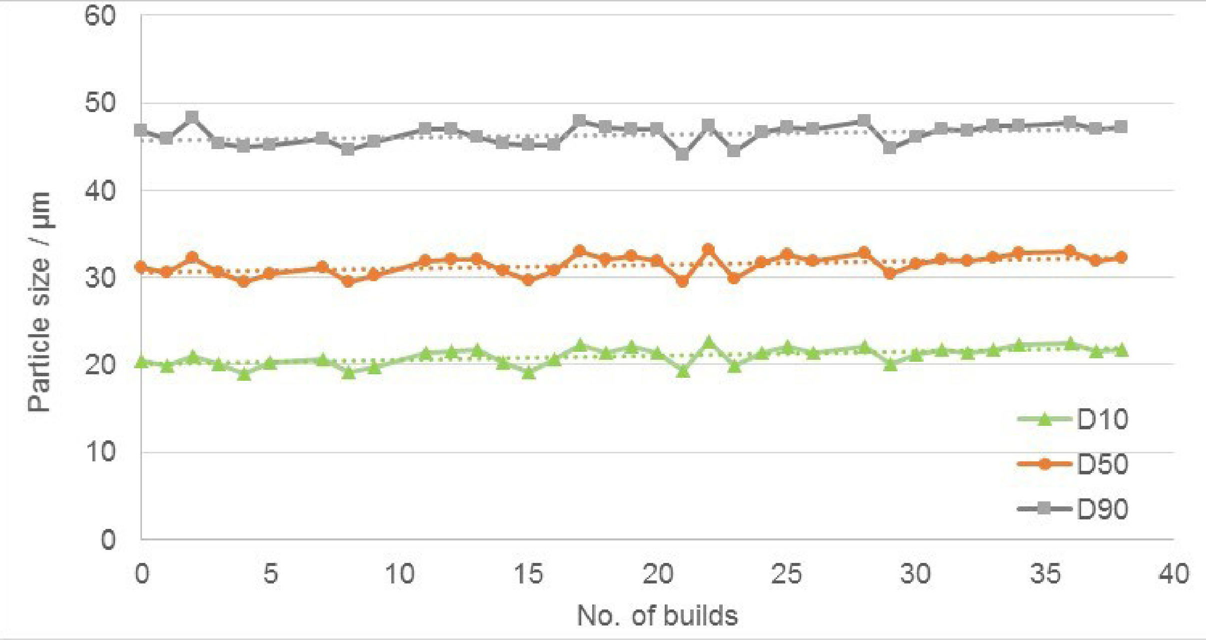

Figure 7. *D10, D50 and D90 values for the metal powder over the period of the re-use study*

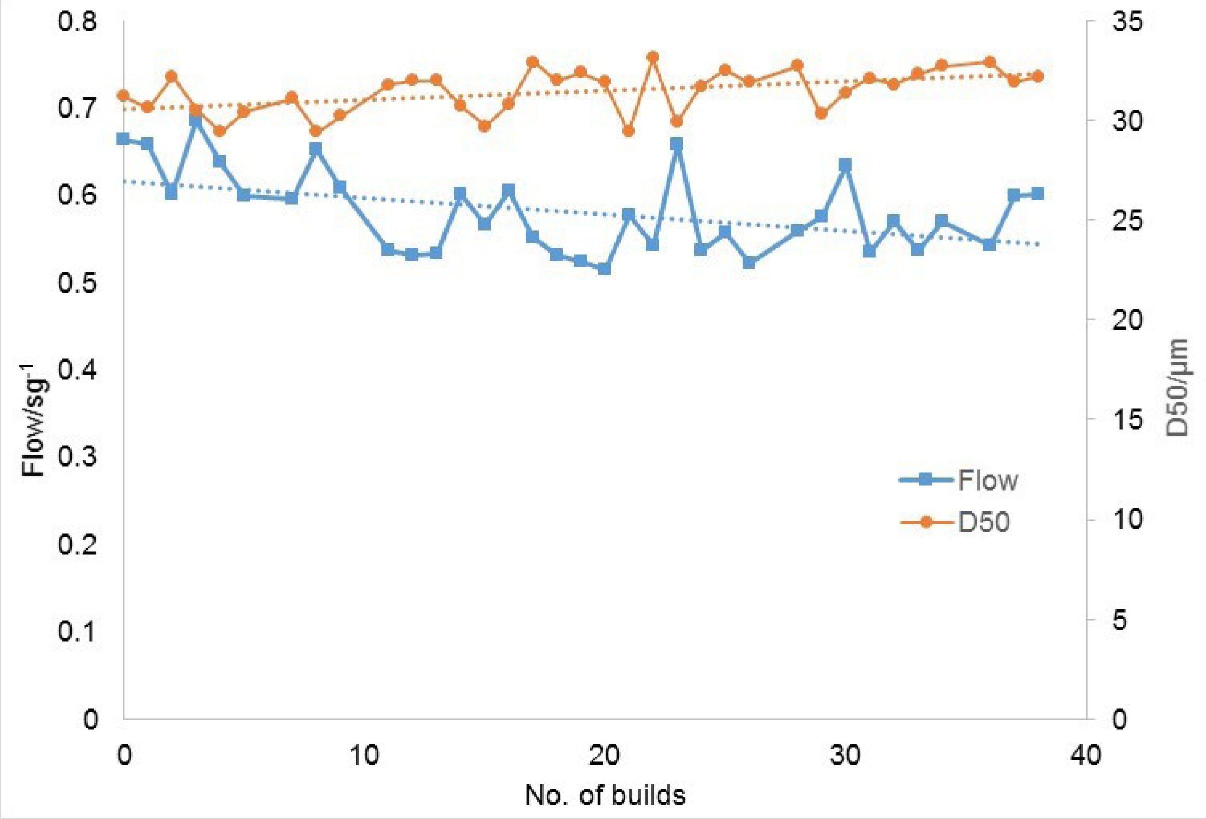

Figure 8. *Powder flow generally increases in speed over the re-use study. As D50 increases so does the flow due to loss of smaller particles*

– smaller particles are being slowly removed most likely by sintering to larger particles. This results in an increase in the Hall flow of the powder. Possible reasons for increased flow speed due to removal of smaller particles are:

- A higher level of smaller particles means more inter-particle interactions and therefore lower flow rates.
- Fewer small particles reduce packing therefore increasing flow.

The virgin powder required a single tap to flow through the Hall funnel, all other powder flowed freely.

There is a general increase in Hall flow speed over the period of the re-use. This is most likely due to reduction in number of smaller particles.

When D50 is compared with Hall flow in Figure 8., it is clear that as D50 increases so does flow speed, highlighting the relationship between the two powder properties. These changes however don't appear to be significant in terms of material parameters or layer spreading.

Powder density

The density of the powder was measured using a helium pycnometer. This indicates whether there are any hollow grains within the batch. There was little change found in the powder from virgin to 38 builds, all values were within 99.397% to 99.158%.

Tensile properties

All tensile bars were heat treated using a vacuum furnace. Bars from builds 1, 12, 18, 24, 31 and 38 were tested. In order to investigate as built surface and machined surface tensile properties, 3 of the test bars from every build were designed with an extra 1 mm diameter to allow for machining, meaning that all 6 bars conformed to the E8 ASTM standard diameter of 3 mm.

The UTS values did not change significantly. An increase in 100 MPa from virgin to build 38 can be attributed to the increase in oxygen and nitrogen levels. A comparison between the 'as built' and machined tensile test bars is shown in figure 10. The machined bars gave higher UTS values, which can be attributed to the smoother surfaces with fewer crack initiation points compared to the rougher 'as built' samples, however an alternative explanation could be that the values for the two different surface finishes are a result of measurement error in the cross-sectional area for the rougher surface which assumes a machined finish.

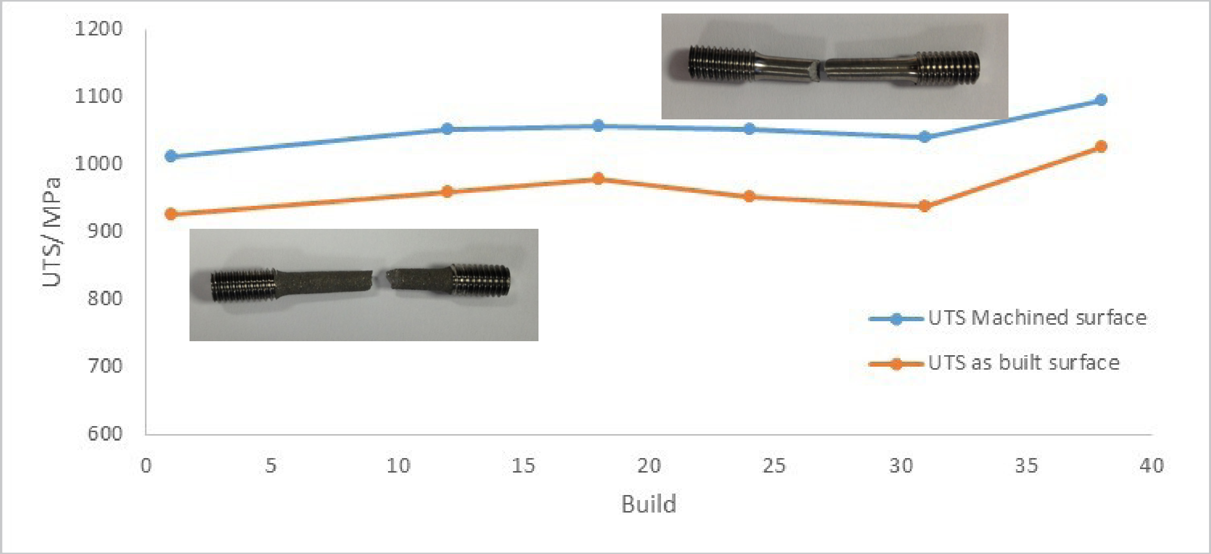

Figure 9. *Upper tensile strength values for the 'as built' and machined tensile bars from builds 1, 12, 18, 24, 31 and 38 showing a n example of each type of pulled bar.*

Build no.	Youngs modulus / GPa		0.2% PS / MPa		UTS / MPa		Plastic elongation / %		R of A / %	
	As built	Machined	As built	Machined	As built	Machined	As built	Machined	As built	Machined
1	103	113	788	839	925	1012	13	7	24	14
12	103	117	849	934	960	1052	14	12	32	30
18	109	116	863	921	979	1056	15	17	30	42
24	105	116	837	918	951	1051	11	7	21	12
31	104	116	823	897	938	1041	9	10	19	18
38	111	119	916	989	1026	1095	15	17	25	47

Table 3. *Tensile analysis results from build numbers 1, 12, 18, 24, 31, 38 for both 'as built' surface finish and machined surface*

Morphology

Qualitative analysis of the titanium powder was carried out using a scanning electron microscope. Virgin powder is highly spherical with a moderate level of satellites and small particles which may be the reason for stunted Hall flow. Figure 13. is an example of a satellite particle in the virgin powder at magnification × 750.

It is clear in the PSD data that smaller particles are removed over the period of the builds, and this is also observed in the SEM analysis of the powders. Other than the loss of smaller particles the powder changes very little, staying spherical, with the occasional misshaped particle most likely ejected form the melt pool or agglomerated next to the weld pool.

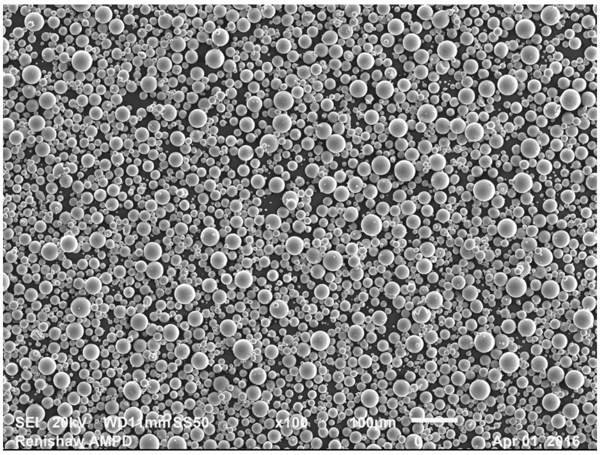

Figure 10. *SEM image of Ti6Al4V virgin powder at × 100 magnification*

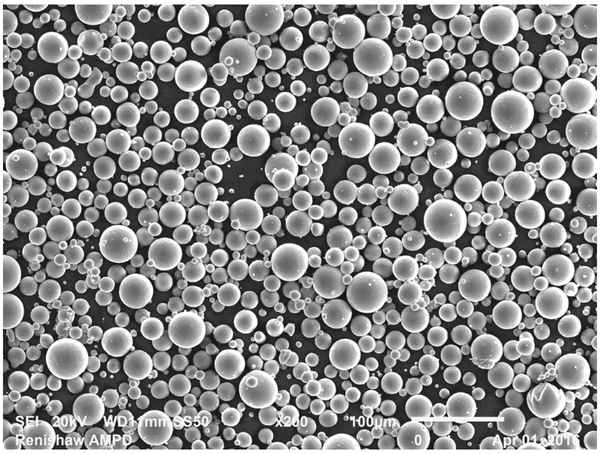

Figure 11. *SEM image of virgin Ti6Al4V powder at × 200 magnification*

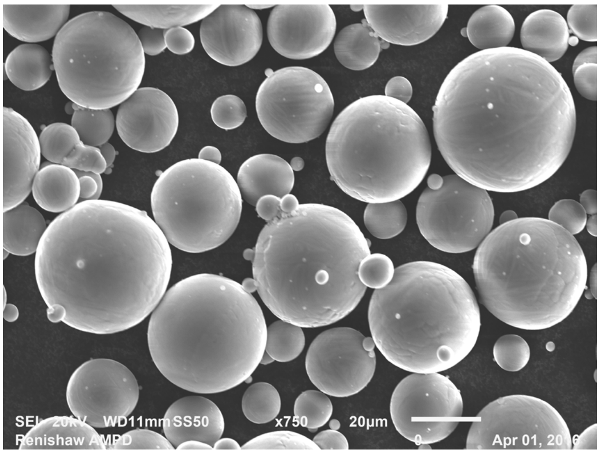

Figure 12. *SEM image of virgin Ti6Al4V powder clearly showing small satellite particles sintered to larger particles × 750 magnification*

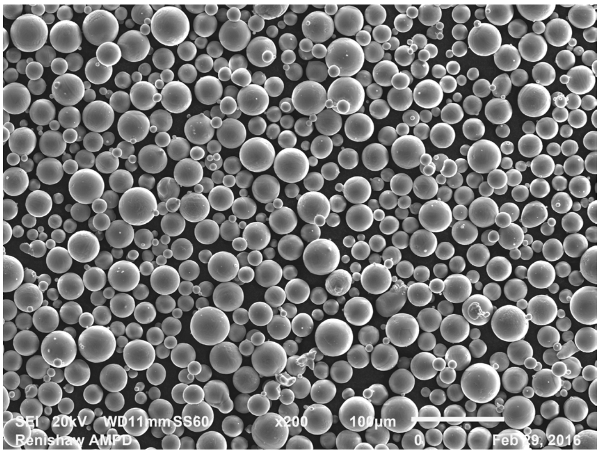

Figure 13. *SEM image of T6Al4V powder after 19 builds. There is a clear reduction in smaller particles and satellites × 200 magnification*

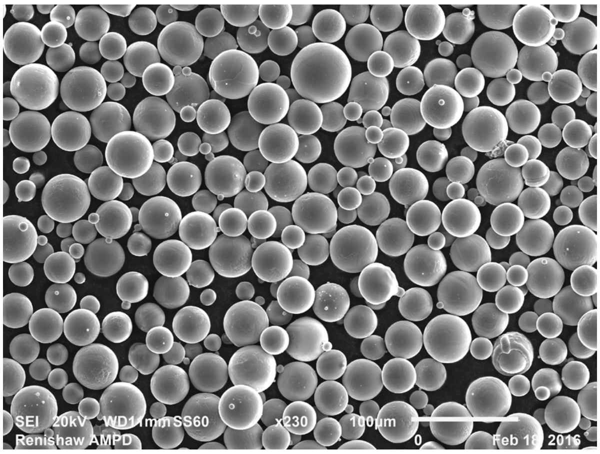

Figure 14. *SEM of Ti6Al4V powder after 38 builds. Particles are still highly spherical with a reduction in smaller particles and satellites compared to virgin powder × 230 magnification*

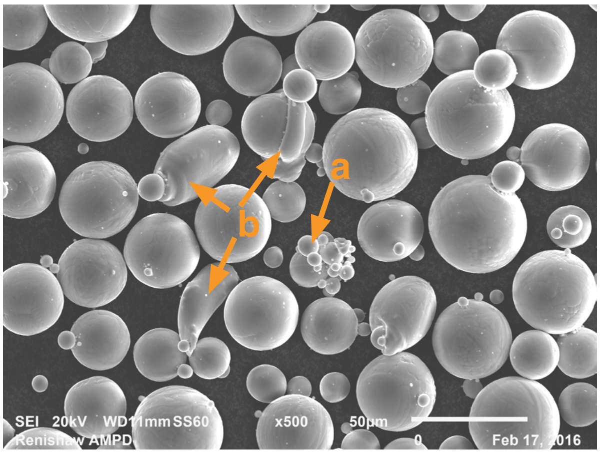

Figure 15. *SEM of Ti6Al4V powder from build 17 showing an agglomerated particle (a) and misshapen particles (b).× 500 magnification*

General conclusions

The changes observed over the period of the two studies do not seem to affect the way that the AM system functions with the powder, therefore the material parameters are still valid for the powder from start to end.

There was a general increase in oxygen and nitrogen levels observed over both studies. These impurities are most likely picked up by particles close to the weld pool which are heated but not melted. The levels of both impurities do eventually reach the maximum allowable for ELI grade Ti6Al4V, however they stay well within the specifications for the more widely used grade 5 Ti6Al4V.

It is likely that under a normal running scenario in which the silo is topped up with virgin powder at regular intervals the levels of oxygen and nitrogen would stay within acceptable boundaries as the new powder blends with the used. This however will require backing up with data.

Flow improves as the number of builds increases, this is most likely due to narrowing of the PSD by gradual removal of smaller particles. Powder morphology does not significantly change over the entirety of the study. Occasional misshapen and agglomerated particles occur within the bulk but at a very low occurrence, and the effect does not seem to be cumulative.

Discussion

The observations gained from this study suggest that there is no requirement to dispose of un-melted Ti6Al4V after it has been cycled around the AM250 system after a limited number of times. This does however depend on the specific requirements of the component material properties, in which case a stringent blending regime may be required for traceability.

The effects of powder re-use will potentially be different for other materials in terms of physical property effects, however because titanium has a high propensity to pick up interstitial impurities, the pickup rates observed can be thought of as a 'worst case' for commonly used metal AM powders.

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