The absorption of moisture by metal powder in a humid environment and the effects on its composition

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ABSTRACT: Selective Laser Melting is a rapid prototyping technology that enables the production of complex geometric parts with customisable material properties. This study aims to investigate whether the environment in which the metal powder is kept, for example a highly humid environment, could influence the properties of the metal powder, and as a result of this alter the mechanical properties of the final component. Three metal powder alloys were analysed for moisture absorption; Inconel 718, AlSi10Mg and Ti6A14V. Of these alloys, the AlSi10Mg samples were analysed more exhaustive using two X-ray spectroscopy techniques to determine if the composition of the material has changed as a result of the exposure to a humid environment. It was found that for the limited humidity exposure applied in this research, the absorbed amount of moisture by the metal powder was less than 0,3% of it's mass. Also, there is no indication that the humid environment has had an influence on the composition of the materials that were exposed to it, because there was a high variability of composition among the particles, especially on the surface of each one.

Key words: selective laser melting, humidity, additive manufacturing, reliability, AlSi10Mg, Ti6A14V, Inc718

1 INTRODUCTION

A lot of research is being done at the moment on achieving fully dense components using Selective Laser Melting (SLM) with an as high as possible build-up rate.

Almost no research is being done on the influence of the environment in which metal powder that is used in SLM is stored on the mechanical properties of the final product. It is possible that moisture diffuses through the containers in which the metal powder is being stored, which might influence the mechanical properties of the final product. In some cases, it might not be possible to maintain a constant environment in which the containers with the metal powder can be stored. To determine if such an environment is necessary, more research is needed in this field.

An example of previous research in the field of SLM is that of Bremen, Meiners and Diatlov [1]; they researched ways to achieve high density AlSi10Mg products, with an as high as possible build-up rate. They managed to increase the build-up rate by 425%. Also, they reduced the distortions caused by the SLM process of a test product from $3mm$ to $0,2mm$ by pre-heating the powder bed. Masmoudi, Bolot and Coddet [2] studied the atmosphere interaction zone during the SLM process; they made a model of this zone, which was verified using experimental data.

This research will help contribute the increasing knowledge of the SLM process, and help it to become a more viable technology.

2 EXPERIMENTAL PROCEDURE

For the research, the National Aerospace Center (NLR) provided the author with $4cm^3$ of powder of three different metal alloys: AlSi10Mg, Inconel 718 and Ti6A14V. These samples came in containers from NLR that had been there for multiple weeks. Before testing, the containers were stored in an air-conditioned room until use.

To measure if the samples contain moisture from production or storage at NLR, the samples are first dried using a moisture analyser. This device heats the sample in a sample pan, and weighs the sample continuously. The metal powder is instantaneously exposed to a temperature of 80 $^{\circ}C$ for 1 hour [3] to evaporate all moisture. The decrease in weight is assumed to be the amount of moisture that evaporates. A small part of the heated powder was kept aside for further research.

After the metal powder is cooled down to room temperature, each material is evenly distributed on the bottom of their own measuring cup, which is then labeled, closed off with foil over the top, the foil punctured with a needle, and put into a climate chamber. The foil is held into place using rubber bands. The foil is used to prevent the metal powder particles from flying away; this is, because inside the climate chamber a fan is present to ensure a uniform distribution of the humidity. A small test sample was used to test if, with the foil on top, the metal powder particles would fly away; this was the case, yet the amount was very small (less than 2% of the powder after 3 days).

After each week in the climate chamber, a sample of about 1,5 gram is taken out and analysed with the moisture analyser to determine the moisture content of the sample. This is done for just over 3 weeks, in total 23 days. 23 days was taken instead of 21, due to availability of the equipment. The sample that was kept aside at the beginning, and so was not exposed to the humid environment, will be referred to as the "0-day sample"; the sample that went into the climate chamber for 23 days and was then analyzed will be referred to as the "23-day sample".

2.1 Equipment

The device used to analyse the amount of moisture in the samples is a moisture analyser; the type is an AND MS-70. It can measure the weight of a sample from 0-70 gram, with an accuracy of 1 milligram. The sample is heated using a halogen lamp, which can control the temperature from 20 to 200 $^{\circ}C$.

To expose the metal powder to a humid climate, a climate chamber is used: a Vötsch VCL 0010. The settings that can be varied are the relative humidity of the air inside, from 20 to 90%, and the temperature, from 20 to 50 $^{\circ}C$. The temperature in the room where the climate chamber is stationed has a temperature of 24 $^{\circ}C$. When the temperature in the climate chamber was set lower than this temperature, the humidity inside the chamber was not able to reach the set humidity; therefore the temperature inside was increased to 25 $^{\circ}C$, after which the humidity was on the requested level of 90%.

To analyse the composition of the metal powder, two X-ray spectroscopy techniques are used; Energy-dispersive X-ray spectroscopy (EDX) and X-ray photo-electron spectroscopy (XPS).
The main difference between EDX and XPS is the depth of the analysis. Whereas EDX is able to determine the composition of a material up to a depth of several 100's of nanometers, XPS only analyses up to a maximum of 10 nanometer depth. As a result of this, EDX is able to measure the overall change in composition of the particles, whereas XPS can analyse the change in the composition of the top layer (which was able to interact with the humid air). The XPS machine used is a Quantera SXM, and the EDX machine is a Merlin Gemini II.

2.2 Material behaviour

Before doing any experiments, possible complications as a result of absorption of moisture by the metal powders will be described.

2.2.a Moisture

In general, the presence of moisture could affect the flow behaviour of the powder when melted, changing the chemistry of the melt pool. The vaporization of the moisture when heated could affect the atmosphere in which the SLM takes place, which affects the surface condition of the powder particles and could influence the properties of the final product.

2.2.b Ti6A14V

The Ti6A14V alloy has an affection for H_2; if the alloy comes into contact with H_2, this causes porosity in the material. Due to the possibility that H_2O could decompose into H_2 and O_2 as a result of the high temperature during the melting process of SLM, problems might arise if water is absorbed by the metal powder. Since it is a reactive material, oxide layers will very likely be formed, unless it is being kept under nearly vacuum conditions; the same goes for the AlSi10Mg powder.

2.2.c AlSi10Mg

AlSi10Mg is an Aluminium alloy that has an affection for oxygen and hydrogen. It is possible that AlH_3 and Al_2O_3 are formed as a result of the high temperature when the metal powder is melted during SLM and the water in the metal powder breaks-up into H_2 and O_2.

2.2.d Inconel 718

Inconel 718 is a nickel-alloy which is heat and corrosion resistant. It contains a number of elements; chromium, titanium and aluminium among others. Due to the corrosion resistance, oxidation of the material is not expected, but moisture absorption by the powder could still influence the environment within the SLM machine.

2.3 Time

The longer the metal powder is being kept in the climate chamber, the more moisture could be absorbed until an equilibrium is reached. Due to the short available time, the length of the experiment was kept to 23 days, which might not be long enough to get reliable results.

3 RESULTS

The samples that went into the climate cabinet were taken out each week for analysis, and were put back afterwards. Each week, a small sample of around 1,5 gram was analysed. Because of the small amount of available material, this was the maximum available amount; the total amount of each powder available varied from 14 to a maximum of 40 gram.

3.1 Moisture analysis

The decrease in weight of the metal powder during heating in the moisture analyser was very low, and in the vicinity of the accuracy of the moisture analyser(1 milligram). Because the decrease in weight is so small, it is hard to determine the exact amount of moisture. However, it can be said that the amount of moisture is low, since the accuracy is not high enough to detect it.

The measurements of the moisture analyser are plotted in figure 1. To give representative numbers in this figure, the moisture percentage is given as the decrease relative to the dry (end) weight. The formula for this percentage is given in equation 1. As can be seen in the figure, the amount of moisture varies from week to week. What effect can cause this behaviour is unknown, it is possible that the moisture that is absorbed varies along the metal powder. For more accurate measurements, the size of the samples has to be increased, to decrease these errors.

$$Moisture\% = \frac{\text{Decrease in weight}}{\text{End weight}} * 100 \qquad (1)$$

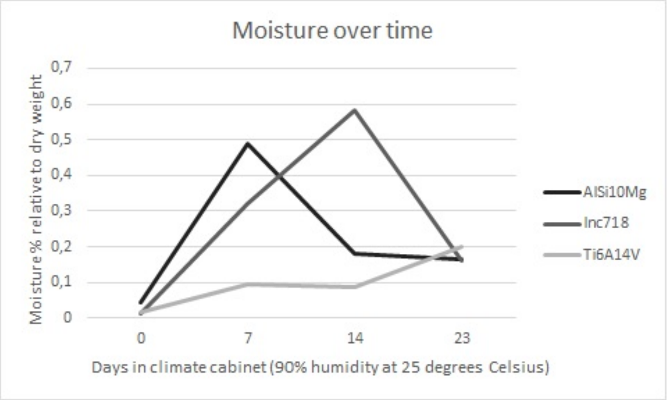

Figure 1: Moisture percentage relative to dry weight

In the graphs that were made using the moisture analyser, a strange pattern arises, see figure 2. The first couple of minutes the mass decreases rapidly, after which it increases and stabilises. This pattern is seen with every measurement, with all three different materials. Two explanations for this effect were considered: it might be possible that something is occurring within the moisture analyser as a result of the sudden increase in temperature, or the moisture analyser is defect in some way. To exclude the second possibility, the measurements on the 14^{th} day were checked with another device, a Thermogravimetric analysis (TGA).

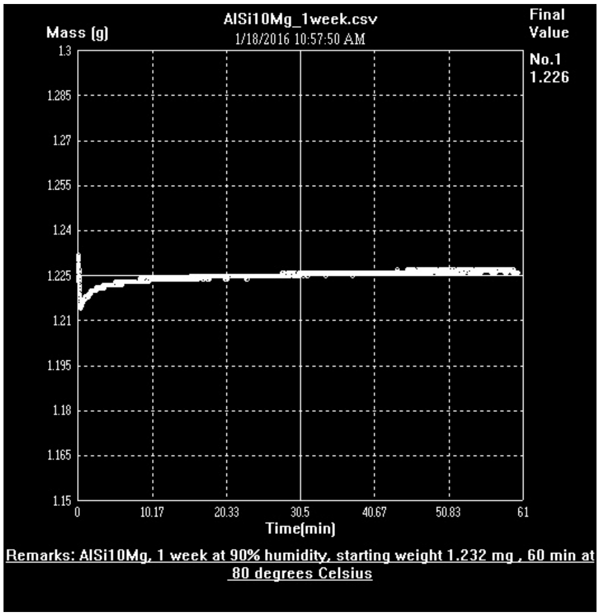

Figure 2: AlSi10Mg measurement moisture analyser

3.2 *TGA procedure*

After the sample was added to the measuring cup of the TGA, some time was taken to wait for the weight of the sample to stabilize before the measurement was started. The temperature was first kept isothermal at 30 $^\circ C$ for 3 minutes, after this, the temperature was raised to 150 $^\circ C$ at a rate of 10 degrees per minute. After this, the temperature was kept isothermal for 30 minutes.

The TGA shows a similar effect to that of the moisture analyser, but instead of a decrease in weight, the weight increases. After some time the weight starts to decrease again and stabilize.

In some measurements, the amount of mass at the end of the measurement was higher than the starting mass, but the difference in increase/decrease in weight was similar to that of the moisture analyser; in the range of 0 to 0,3%. It could be that vibrations produced by the air flow within the TGA cause these results.

3.3 *EDX*

Since the EDX and XPS analysis are both very expensive, both analysis were conducted on two samples of 1 material. AlSi10Mg was chosen, because the material started to form lumps of material, which could affect the flow behaviour of the material and makes it unusable; these lumps are shown in figure 3.

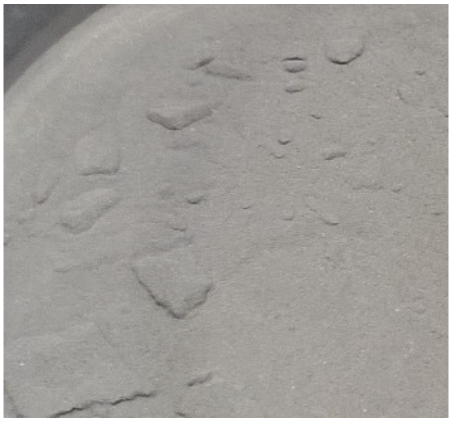

Figure 3: AlSi10Mg powder after 23 days

The EDX analysis shows that the composition of the samples varies largely with each particle, and also over the surface of each particle. To be able to analyse the differences, boxplots were made to give a representation of this. In figure 4 a boxplot is seen of the relative mass percentages of oxygen and carbon, for both the 0-day sample and the 23-day sample.

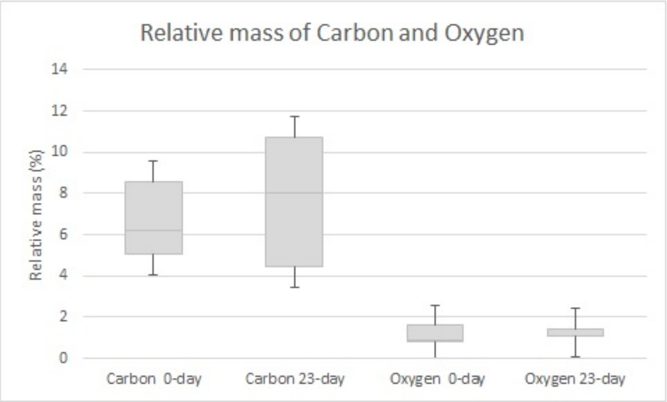

Figure 4: Boxplot Oxygen and Carbon

There is no reason to conclude that the composition of the material has changed, based on the results. This is largely, because of the large variation in the composition of the particles.

Figure 5 shows some of the particles of the 0-day sample. As can be seen, some particles are deformed and not round, which is not preferable for SLM. Also, smaller particles are attached to the larger particles. The size varies a lot. The largest particle found was about 150 μm, which is 3 times the layer thickness of 50 μm that is used by NLR for most printing jobs.

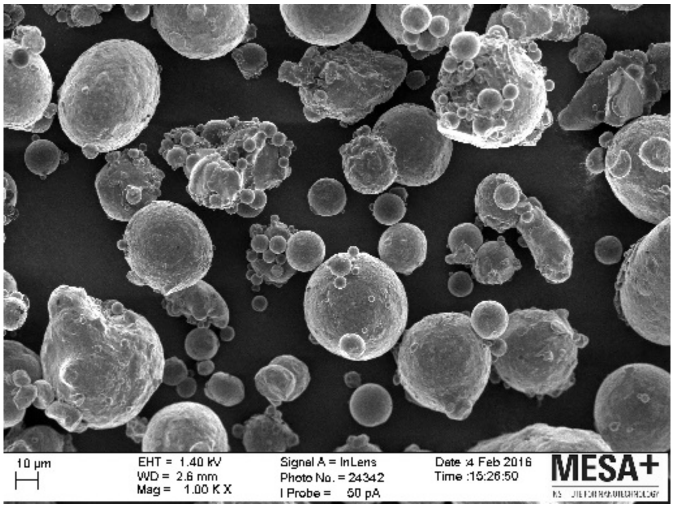

Figure 5: AlSi10Mg particles SEM micrograph, 1000x magnified

3.4 XPS

Using XPS, the first few nanometer of the particles were analysed and compared to each other.
To determine the variance in the samples, 5 analysis were conducted and with this, the standard deviation was calculated. The relative amount of the 5 elements that were mostly present is presented in table 1 for both samples. Also, small amounts of sulfur were found in both samples with the XPS, this could be caused by a contamination or a production error. Since it did not show up on the EDX, the overall amount of sulfur seems to be negligible.

Table 1: AlSi10Mg composition XPS

Element sample	C	O	Mg	Al	Si
0-day composition (%)	13,66	57,58	5,46	16,85	6,45
Standard deviation 0-days sample	1,41	0,94	0,39	0,66	0,16
23-days composition (%)	8,26	62,29	4,94	18,94	5,58
Standard deviation 23-days sample	1,19	0,83	0,46	0,37	0,11

The amount of carbon in the samples is quite high for both the XPS and EDX analysis, especially since carbon is not part of the composition of AlSi10Mg. How the carbon got in the sample is unknown, it could be that this is a production error, or the result of a contamination during storage or while testing. Because XPS only looks at the first few nanometers, the high amount of oxygen can be explained by the formation of an oxide layer. It is present in both cases, but it has not increased significantly enough to conclude that something has changed.

With XPS, the chemical state of the materials is analysed. The carbon that is present is mostly carbonate (CO_3^{2-}), and the oxygen has a value that corresponds with hydroxides (OH^-).

4 DISCUSSION

During the process, multiple points of discussion arose, these will be discussed below.

4.1 The sample size

Since the amount of moisture was very low, the amount of mass required to accurately measure the moisture percentage of the samples using the moisture analyser needed to be over 20 gram [4]. The sample size was only 1,5 gram which led to inaccurate results. However, the differences were so small that can be concluded that the amount of moisture that was absorbed is low. Also, only 1 measurement was conducted each week, this way it is not known how much variation there is between measurements.

4.2 The timescale

The timescale was taken to be 23 days, which is relatively low, because the containers are usually stored for much longer amounts of time. A longer timescale was not possible due to time issues.

4.3 Days in storage

The samples that were provided by NLR were placed in sealed containers, of which it is not known if liquid is able to diffuse through. Also, the amount of time the samples had been at NLR is unknown, therefore it could be that the samples were already exposed to a humid environment for a long time. Also, it is unknown how long the material has been in storage at the supplier. More accurate testing could be done by doing the same tests, but with samples that come directly from the supplier.

4.4 *Heating*

Based on literature, [3], it was chosen to set the temperature for the moisture analyser at 80 °C. When tests were conducted which were similar to that of the TGA (the temperature was increased to 150 °C in 12 minutes, and then kept isothermal for 30 minutes), the decrease of mass of the sample was much larger. It might be possible that the taken approach does not evaporate all the water every time, which could explain the differences in moisture percentages over the weeks, but this seems farfetched.

4.5 *Accuracy equipment*

The accuracy of the moisture analyser was reported to be 1 milligram. Due to a special option in the configuration, it is possible to increase the accuracy to 0.1 milligram, giving a much more accurate result of the moisture percentages. Sadly, this option was discovered only after all measurements had been conducted.

4.6 *Humidity*

The relative humidity of the air was set at 90%; this is higher than the humidity at NLR where the containers are stored in an air conditioned room with a humidity between 50 and 60%, but because time was limited, the highest possible humidity was chosen to get an as high as possible absorption of moisture within the available time.

4.7 *Limitations*

Different values for the humidity and storage temperature were left out of the research, due to the limited amount of time. Also, due to the high cost of Selective Laser Melting powder and the possible contamination of the machine, it was not possible to compare the mechanical properties of parts of which the powder was exposed to a humid environment to those that weren't exposed to a humid environment.

5 CONCLUSION

This research concludes that the amount of moisture that is absorbed by metal powder (for AlSi10Mg, Ti6A14V and Inconel 718) is small, but not negligible. Due to the variation in the results, the exact amount of moisture was not computed. There is, based on the EDX and XPS analysis of the AlSi10Mg sample, no evidence that suggests that the composition of the metal powder has changed as a result of the exposure to the humid environment. However, it is not possible to unambiguously conclude that the humid environment does not affect the powder at all due to the large variation in the composition of each sample. The material provided by NLR varies a lot, and its particles are often deformed or larger than the layer thickness that is used for making components from the powder, which is a big issue. Despite the effort put into this subject, this research only focuses on a humid environment for a relative short timescale. Other environments, such as a salty environment (for example if the metal powder is stored on a ship for printing spare parts) are not covered within this research, and are interesting fields to conduct research in, in the near future.

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