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REMOVAL OF COPPER POWDER FROM ELECTRON BEAM MELTING (EBM) PROCESSED PARTS

ISE – 789 ADVANCED METAL ADDITIVE MANUFACTURING

FINAL PROJECT REPORT

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INTRODUCTION :

During the last couple of years, digital manufacturing of components based on layer-by-layer fabrication has developed from rapid prototyping to additive manufacturing[Konner]. In contrast to conventional fabrication technologies, AM offers much more design freedom. The design of the components is not restricted by the production method, one could design individual parts with a high complexity, like cellular structures, complex internal structure or cooling channels. In addition topology optimization could be utilized to make lighter yet structurally strong parts. This offers many advantages: complex geometry, weight reduction, short lead time, integration of functions, etc [6].

Electron beam melting(EBM) belongs to the umbrella of the additive manufacturing technologies. The components are built layer by layer within a powder bed by selectively melting the powder with a high power electron beam. It is similarly structured to the selective laser melting in terms of the process on a broader scale, but in contrast to selective laser melting (SLM), which can be used for metals, polymers and ceramics, the application field of the electron beam is restricted to metallic components since electric conductivity is required. On the other hand, the electron beam works under vacuum conditions, can be moved at extremely high velocities and a high beam power is available[6].

Electron beam melting was commercialized in 1997 by Arcam AB Corporation in Sweden. The process of electron beam melting usually result in the production of dense parts. The process makes use of electrons as an energy source, which is then passed through a series of lenses, which help to focus, shape and deflect the beam in accordance with the process parameters and the design of the component itself. An electron beam can be focused and moved inertia-free by electromagnetic lenses. Thus, the electron beam reaches velocities of up to 105m/s within the building area, [6] i.e. the beam is able to jump nearly instantaneously from point to point. Hence, with an electron beam innovative heating and melting strategies can be realized. On the other hand, vacuum conditions are necessary as it eliminates the impurities and yields high strength properties of the material. Vacuum also facilitates the use of highly reactive metals, also the high build temperature provides good form stability and low residual stress in the part.

Metal 3D printing generally requires a lot of work, even after the part has been printed. The parts need to be post processed to make them ready for the next stage of machining to produce the finished parts. Not only do supports need to be removed, but excess powder needs to be cleaned off the part – and that's easier said than done, as metal 3D printing powder is hazardous to handle, for one thing, and for another many parts are designed with channels and voids where powder can get trapped. Cellular metals, also known as metal foams, can be explained as solid metals exhibiting cellular structures that form voids called pores. In general, there are two broad categories of metal foams, stochastic and non-stochastic geometries. [7] Briefly, stochastic foams have random variations in the shape and size of the cells, whereas in contrast, periodic cellular structures have repeating lattice structures and can be categorized by their shapes and sizes. Powder removal is a critical phase of Additive Manufacturing for application as stated by Romain Gérard, Additive Manufacturing Engineer at CERN. He also stated that "We observed that powder residues, that are subsequently sintered during heat treatment, act like sponges by trapping gases and releasing them at a very low rate". The sintered powder that remains in the built part cavities and channels increases the weight of the part and needs to be removed for the part to continue its post processing. The concept of removal of sintered and even free powder from the post built parts, is a dicey concept and is fast being researched by many additive manufacturing companies. Usual tactics involves chemically etching out the powder, as powder having a larger surface area exposed, are acted upon by the etchant in a preferential manner, physical methods like mechanically rotating the parts in multi axes, in 3D orientation are also employed, the more recent advanced techniques involve the usage of vibration frequencies to aid in the removal of the sintered powder, also utilizing the

## RAW MATERIAL SETUP AND CHARACTERISATION :

Being a powder bed fusion type metal additive manufacturing build method while using an electron beam as a source of energy transfer, the process requires metal powder as the feedstock. Which directs the discussion to the fact that the properties of the final part can be controlled by the changing the powder characteristics, like powder size distribution (PSD) and powder morphology strongly influence the flow and the packing of the powder and thereby the density of the part (1 - 5). To begin with the process, the electron beam sinters the powder bed to increase the electrical conductivity of the powder to prevent smoking (6). This sintered powder in most of the cases is

rather hard to remove. This problem becomes more severe in parts with intricate internal channels and cavities. Post – processing and powder removal has always been a challenge in the additive industry. Degree of sintering directly influence the difficulty for powder removal. In this case, the team used non – destructive mechanical and chemical techniques to remove copper powder from internal cavities. The powder size distribution (PSD) of the high purity copper used to manufacture the experimental parts ranged from 19.65 microns – 69.55 microns for volumetric measure (Fig 1) and from 3.80 microns – 36.24 microns for number measure (Fig 2). LECO analysis concluded that the feedstock powder consisted to Oxygen at 450 ppm and Hydrogen at 1 ppm, which testifies copper powder as high purity.
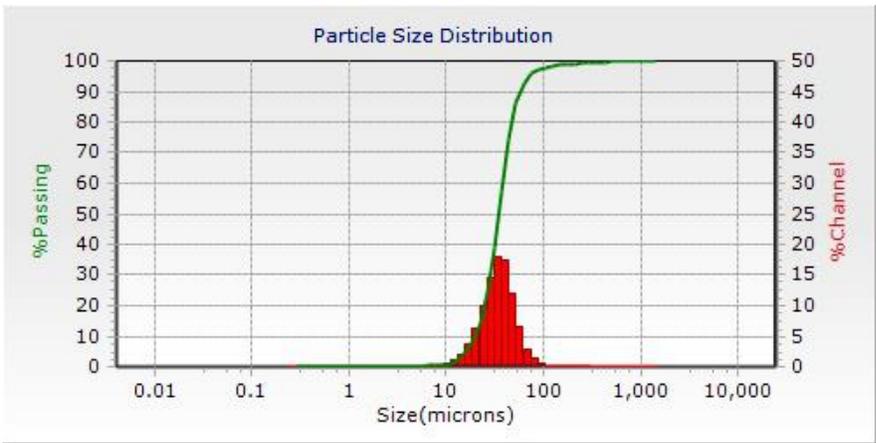
FIG 1: VOLUMETRIC POWDER SIZE DISTRIBUTION OF COPPER POWDER USED FOR THE PART BUILD
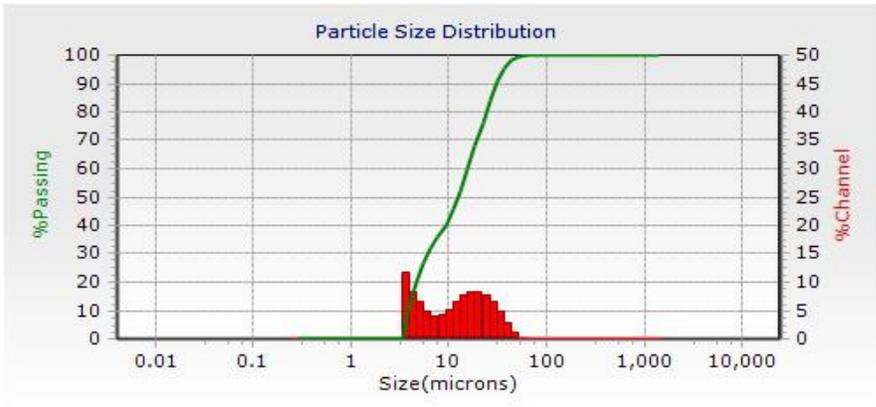
FIG 2: NUMBER POWDER SIZE DISTRIBUTION OF COPPER POWDER USED FOR THE PART BUILD

The final produced part is a hollow cylindrical block with three differentiated levels and a small concentric opening (Fig 3 – 4).
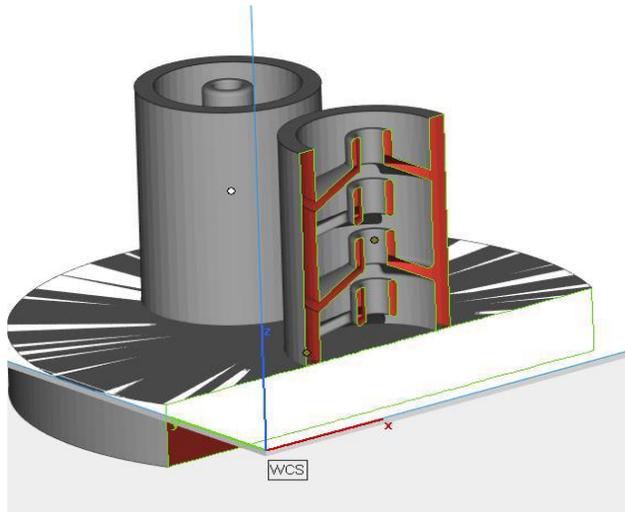

FIG 3: SECTION VIEW OF THE FINAL PART   FIG 4: FINAL MANUFACTURED PART

EXPERIMENTAL PROCEDURE :

Copper parts with sintered material exposed were used to gauge the effect of the removal process. An example of an unprocessed specimen is depicted in (Fig 5). This was done for two main reasons: characterizing the material removal from internal cavities involved time consuming processes that inhibited rapid experimentation, and these parts were readily available as failed prints for a related project.

These parts were made of high purity copper powder, with a large sheltered region on either side of the part. Two sets of samples were used with different powder conditions with the primary difference being the degree to which the powder was sintered.

FIG 5: **EXAMPLE OF A SPECIMEN BEFORE ULTRASONIC TREATMENT.**

A chemical process with agitation was chosen as the method for powder removal. An ultrasonic cleaner was used as the source of agitation as flow would be significantly impeded by part geometry in any other agitation method. Ultrasonic energy has the benefit of conducting through the part, providing agitation to the cavities in addition to in free solution. A Branson 1510 was used to conduct the experiments, with a power output of 70 watts at a frequency of 42 KHz. Specimens were placed in glass beakers to contain the testing fluid. Direct application of ultrasonic energy to the parts was not investigated in these experiments. Since parts were made of copper, the active fluids were chosen to be especially effective on copper. One mixture consisted of a copper ammonia complex solution often used in etching. This solution has been shown to be effective at attacking copper under ultrasonic agitation in literature[9].

The specific chemistry used in this experiment was 1 molar copper sulfate and 15% ammonium hydroxide in water. The active ion in this etchant is the cupric-ammine complex, which is regenerated readily when exposed to oxygen. This etchant actually increases in activity as it dissolves more copper and can be regenerated and reused by dilution with ammonium hydroxide solution. Citrinox, a commercially available copper bright etch consisting of citric acid and glycolic acid was also used since it is often used as a cleaner for copper parts. These solutions were compared to parts in water or ethanol. Water and ethanol were used as comparison solutions due

to their use as part of a typical cleaning process for parts. While the temperature was not closely controlled during the experiment, the tank was monitored during testing and it was found that the tank stabilized at approximately 45°C after about 1 hour of sonication.

RESULTS AND DISCUSSION :

It was predicted that the use of ultrasonic energy in a chemically aggressive environment would be sufficient to loosen and remove EBM sintered powder. Sintered powder consists of individual powder particles fused together by necks of material joined through diffusion. In the EBM process, these necks are typically relatively small and mechanically weak such that powder can be later removed from the part during the cleaning process. Chemical attack of these sintering necks was expected to reduce the size and strength of these bonds, allowing for the powder to be removed through relatively light treatment.

Ultrasonic energy is often employed in high cycle fatigue testing as a method of applying a mechanical load capable of propagating cracks and causing failure at loads much lower than the tensile strength. When applied in an aqueous environment, ultrasonic waves induce cavitation in the fluid. The collapse of ultrasonically induced cavities on surfaces is often used to clean parts in many industries. When these cavities collapse, they impart energy to the surface by creating a high pressure jet of water [8]. Over extended periods, these jets can cause abrasion, even to robust metallic parts such as stainless steel tank walls. The combination of ultrasonic fatigue effects caused by the ultrasonic energy, and the abrasion of ultrasonic cavitation was predicted to loosen and remove powder from the parts.

FIG 6: SPECIMENS TREATED WITH ULTRASONIC AGITATION IN TAP WATER. LIGHTLY SINTERED POWDER TREATED FOR 6 HOURS (LEFT), AND HEAVILY SINTERED POWDER TREATED FOR 9 HOURS (RIGHT).

The effect of 6 hours of ultrasonic energy in water can be seen in (Fig 6). Water alone was able to cause a significant loosening of the lightly sintered powder from the part. Light handling after the part was removed from the ultrasonic cleaner resulted in much of the powder falling out of the cavity, primarily in small clumps. The more heavily sintered part was more impervious to ultrasonic energy alone. Even after 9 hours of agitation, only a small amount of powder was removed. This effect was only observed due to the light dusting of very fine copper dust in the bottom of the beaker that accumulated over the 9 hour period.

FIG 7: SPECIMENS TREATED WITH ULTRASONIC AGITATION IN ETHANOL FOR 6 HOURS. LIGHTLY SINTERED POWDER (LEFT) AND HEAVILY SINTERED POWDER (RIGHT).

Due to concerns about the absorption of water by the parts, ethanol is used in the current cleaning of parts instead. Ethanol was therefore chosen as a low activity fluid for testing. As shown in (Fig 7), neither sintering condition was significantly affected by ultrasonication in ethanol. In comparison to the water specimens, the apparent importance of the cavitation effect can be observed. This effect could be attributed to a difference in the activity of cavitation in ethanol as compared to water. The water used in this experiment was tap water, which contains some quantity of dissolved salts and minerals. These solutes can act as nucleation sites for the cavities formed during ultrasonication, increasing the mechanical effect of the cleaning process. The ethanol used was 200 proof, laboratory grade alcohol, lacking significant amounts of solutes to act as cavity nuclei. As both conditions were subject to the same degree of direct vibration from the ultrasonic transducers, it can be extrapolated that these vibrations have little importance in the removal of the powder in these experiments. One apparent effect of the ethanol treatment is the discoloration of the powder in the lightly sintered specimen. During the drying of the sample in a fume hood following the test, it was observed that the sintered powder turned black. This discoloration is expected to be cupric oxide, the most common oxide of copper.

Ultrasonic energy can increase the kinetics of chemical processes by increasing the rate at which reactive components can make it to a surface. Jets caused by ultrasonic cavitation can result in high reaction rates at metal surfaces, an effect which can greatly increase etch rates of metals in aggressive environments[9]. Additionally, ultrasonic energy provides agitation in confined environments far better than typical agitation techniques such as mixing or nozzles, especially important for the attack of powder in internal cavities or for the etching for sintering necks inside the sintered powder. A possible effect of the combined action of mechanical agitation and chemical attack is stress corrosion cracking. This is an effect that should generally be avoided, though in this case it may in fact be favorable. The presence of an aggressive environment when a part is under mechanical load can result in easier cracking and overall embrittlement of the part. In the context of the removal of a sintered powder, the presence of an aggressive environment could reduce the necessary mechanical load to break down the powder, even without significant dissolution taking place.

FIG 8: **LIGHTLY SINTERED SPECIMEN TREATED IN CITRINOX CLEANER FOR 6 HOURS.**

The first aggressive environment chosen for testing as the chemical detergent Citrinox. This solution consists of a mixture of citric acid and glycolic acid, which lightly attacks the surface of copper, resulting in a bright etched finish. This solution is currently in use to clean parts of metal additive machines, including the copper build plates used to produce these parts. The apparent effect of this solution can be seen in (Fig 8). The final result was quite similar to the specimens testing in tap water. Lightly sintered powder was removed from the part fairly effectively after 6 hours. Much of the powder remaining in the part was one large chunk which was loose but trapped by the internal geometry. The additional effect caused by the addition of Citrinox was not particularly significant, though the parts were overall less discolored than equivalent tests in tap water.

A solution of copper sulfate and ammonium hydroxide was used to induce a very aggressive chemical environment. (Fig 9) shows the drastic effect this etchant had on the specimens. After 6 hours of treatment, complete removal of powder was observed in the lightly sintered specimens. This solution was the only treatment that had a noticeable effect on the heavily sintered powder. Between 1 and 2 mm of material was removed from the heavily sintered parts over 9 hours, with some apparent powder being present in the bottom of the beaker during the test. This indicates that it was not only the aggressiveness of the etchant that removed the powder, the agitation was able to remove the powder before it was completely dissolved into solution. This suggests that the attack of the sintering necks was at least partially responsible for the success of this treatment.

FIG 9: SPECIMENS TREATED WITH ULTRASONIC AGITATION IN COPPER-AMMONIA COMPLEX SOLUTION. LIGHTLY SINTERED SPECIMEN TREATED FOR 6 HOURS (LEFT), AND HEAVILY SINTERED TREATED FOR 9 HOURS (RIGHT). HEAVILY SINTERED PART AFTER 8 HOURS OF TREATMENT PICTURE BOTTOM.

The drawbacks of this treatment are apparent from the images shown in (Fig 9). Significant discoloration was observed on both parts, likely due to the formation of copper oxide from the exposure of wet fresh surfaces to air following the test. This coating was temporarily removed with a rinse in a dilute ammonium hydroxide solution, but the discoloration reappeared after several hours. Dark blue copper-ammonia solution continued to seep out of the heavily sintered powder for several hours after the test. This was taken to be an indication that significant penetration of the powder had occurred, though it is also possible that the solution had penetrated into the part as well.

A crack was observed in the lightly sintered part following the test. It is unclear whether that crack was present at the start of the test, or whether it formed during the treatment. There exists the possibility that the combined action of the ultrasonication and the copper-ammonia solution could result in cracking. One reason this solution was chosen was the tendency for copper

to crack in similar solutions. It was predicted that this effect would be beneficial for the breaking of sintering necks.

The control of solution chemistry for this etchant is expected to be critical to producing the desired outcome. The etchant actually increases in aggressiveness as it dissolves more copper ions. If the solution absorbs too much copper for the ammonia concentration to be able to hold in solution, a sludge of brown copper oxide will begin to form. This was observed in the bottom of the beaker at the end of the 9 hour heavily sintered specimen test. It is likely that a lower initial copper concentration would be preferable for the removal of powder to prevent this from occurring.

REFERENCES

1. A. Simchi, The Role of Particle Size on the Laser Sintering of Iron Powder, Metall. Mater. Trans. B, 2004, 35(5), p 937–948

2. D. Manfredi, F. Calignano, M. Krishnan, R. Canali, E.P. Ambrosio, and E. Atzeni, From Powders to Dense Metal Parts: Characterization of a Commercial AlSiMg Alloy Processed through Direct Metal Laser Sintering, Materials, 2013, 6(3), p 856–869

3. E.O. Olakanmi, R.F. Cochrane, and K.W. Dalgarno, A Review on Selective Laser Sintering/Melting (SLS/SLM) of Aluminum Alloy Powders: Processing, Microstructure and Properties, Prog. Mater Sci., 2015, 74, p 401–477

4. J.A. Slotwinski, E.J. Garboczi, P.E. Stutzman, C.F. Ferraris, S.S. Watson, and M.A. Peltz, Characterization of Metal Powders Used for Additive Manufacturing, J. Res. Nat. Inst. Stand. Technol., 2014, 119, p 460–493

5. A.T. Sutton, C.S. Kriewall, M.C Leu, and J.W. Newkirk, Powders for additive manufacturing processes: characterization techniques and effects on part properties, in Solid Freeform Fabrication 2016: Proceedings of the 27th Annual International Solid Freeform Symposium, 2016, p 1004–1030

6. C. Körner (2016) Additive manufacturing of metallic components by selective electron beam melting — a review, International Materials Reviews, 61:5, 361-377, DOI: 10.1080/09506608.2016.1176289

7. Hasib, H., Harrysson, O.L. & West, H.A, Powder Removal from Ti-6Al-4V Cellular Structures Fabricated via Electron Beam Melting, JOM (2015) 67: 639, https://doi.org/10.1007/s11837-015-1307-x

8. Mason, T J, and Peters, D. Practical Sonochemistry: Power Ultrasound Uses and Applications. United Kingdom, Elsevier Science, 2002.

9. Norkett, J., & Willcox, J. (2017). US20170058379A1. United States. https://doi.org/10.1037/t24245-000