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ADDITIVE MANUFACTURING OF COPPER BY 3D EXTRUSION

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Abstract. *This work aims to produce pure copper samples by 3D extrusion of highly viscous pastes. Additive Manufacturing enables the fabrication of metallic materials with significant advantages to the industry. In this project, the copper powder was mixed with a binder solution to form metallic pastes. Five compositions were tested, using different aqueous solutions as binders and varying powder/liquid mass ratios. Two different methods were used to create a green part: paste deposition followed by cold compaction and 3D printing by paste extrusion. The first approach aims to determine the best paste composition to achieve suitable printability and mechanical strength in the final parts. In the printing technique, the prototype is autonomously created from a Computer-Aided Design by paste extrusion. In order to enable printing, the paste should be in a short range of viscosity and flowability, as it requires rheological properties that allow extrudability and layering. After printing/compaction, thermal treatment was applied to remove the binder and to sinter, bonding the copper particles. Once produced, the samples were characterized regarding crystal structure, porosity, microstructure, Vickers microhardness, and compressive strength. This microstructural investigation enables comparison between printed and compacted dies and among different paste compositions, while providing an insight into the potential of 3D extrusion-based Additive Manufacturing of copper.*

Keywords: *additive manufacturing, 3D extrusion, cold-compaction, copper, microstructural investigation.*

1. INTRODUCTION

Copper, one of the earliest metals utilized by humans, has been crucial to society since the Bronze Age. Its exceptional properties, including high thermal conductivity (398 WK/m at 27°C), low electrical resistivity (16.730 nΩm at 20°C), and considerable corrosion resistance make it one of the most cost-effective material to meet thermal, chemical, and electrical requirements. Those advantages alongside the relatively low density (8.89 g/cm³) and high ductility explain the wide presence of copper from ordinary uses to ground-breaking aerospace, electrical, and many other applications (Davis and ASM International, 2001). In those innovative scenarios, however, complex geometries and special properties are often needed, which requires new and suitable fabrication methods.

As one of the most promising techniques to supply current needs, Additive Manufacturing (AM) has emerged as a 3-dimensional layer-by-layer production process, widely known as 3D printing. It has revolutionized engineering by enabling the creation of highly complex structures while simultaneously addressing concerns related to material waste and lead-time reduction. Among the various approaches available for metal printing, one of the most affordable and feasible is metallic paste extrusion followed by sintering slightly below melting temperature. The extrusion method is based on the deposition of a material layer by applying pressure and forcing the material through a nozzle. This process offers several advantages, as it reduces the need for expensive and high-energy-consumption equipment (Cañadilla et al., 2022).

The thermal energy dissipation of copper also imposes difficulties on printing methods under fusion, making the 3D paste extrusion a suitable approach for copper. Additionally, it stands out for its ability to produce a more isotropic microstructure than fusion-based layering processes. Copper exhibits a high anisotropy due to its face-centered cubic microstructure, which can be noticed by its elastic modulus varying from 21 GPa in one crystallographic direction to 77 GPa in the other. Then, this technique might hold the potential to produce copper with enhanced isotropic mechanical properties (Davis and ASM International, 2001).

In this context, the present study aims to explore and analyze the unique material properties generated by the 3D paste extrusion of copper. We seek to contribute valuable insights that can propel industrial-level widespread adoption of this advanced manufacturing method, simultaneously increasing sustainability and innovations in the productive chain.

2. METHODOLOGY

2.1 Materials

The materials used in the production of the different copper sample groups were Metallic Copper Powder with a concentration of 99.9% according to the producer (Dinâmica, Batch 122780), Carboxymethylcellulose (CMC, Synth, Batch 218137), Polyvinyl Alcohol (PVA, ACS Científica, Batch 202209139), Polyethylene Glycol (PEG, Labsynth, Batch 216139), Oleic Acid with a 90% technical grade (Sigma-Aldrich, Batch 364525), and distilled water.

2.2 Paste production

Initially, two paste compositions were tested using the 88/12 mass ratio of copper powder and ligand. The two binders were aqueous solutions, one with 2 wt.% of PVA and another with 1 wt.% of CMC. The binder solutions were produced by dissolving the binder powder in water at 80°C on a heating plate under a mechanical stirrer. The pastes, in individual 5 g-sample portions, were blended mechanically until homogeneity. A 0.001 g-precise balance was used for all the procedures. In addition, new ligand types were produced, one aqueous solution with 7.7 wt.% of PVA and 3.5 wt.% PEG and the other with 2 wt.% of CMC. Due to the higher solution viscosity, a higher amount of binder solution (20 wt.%) was added to the copper powder. The PVA+PEG paste was produced with Oleic-Acid-coated copper powder to enhance metal dispersion. To achieve suitable printability, the binder solution/copper proportion was increased to 60/40 in the 3D extruded dies.

Table 1: Copper paste compositions.

Group	Binder	Powder/Binder, wt.%	Fabrication
CuPva880	PVA 2%	88/12	Cold-compaction
Cu1Cmc880	CMC 1%	88/12	Cold-compaction
CuPvaPeg980	PVA 7.7% + PEG 3.5%	80/20	Cold-compaction
Cu2Cmc980	CMC 2%	80/20	Cold-compaction
Cu2Cmc980-3D	CMC 2 %	60/40	3D extrusion

A portion of each paste was left resting on a test tube for days, to identify if a phase separation would occur, which could harm the extrusion process. The PVA had the worst performance, separating the clean liquid from the powder, the CMC remained the most homogeny, and the PVA+PEG was an intermediary.

2.3 Cold compaction

Although the main focus of this project is 3D paste extrusion, the cold compaction method will first be used to allow characterizing the samples. As stated by Cañadilla et al. (2022), the AM technique consists of "the consolidation of a 3D-printed powder compact", which explains the choice of compaction method as a reference. This approach allows not only the selection of the most suitable compositions for 3D printing but also provides a comparison between the two fabrication techniques. This initial method consists of depositing the pastes in a 10 mm-diameter cylindric mold and then compacting under high uniaxial pressure, yielding "green samples".

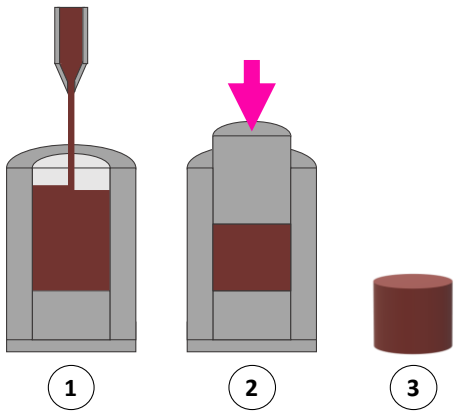

Figure 1. Cold compaction method.

Five pieces of each composition were produced, with an approximate height of 10 mm. Notably, this method tolerates a broad range of paste rheology, which contrasts with AM requirements of extrudable and layer-construction pastes ability. Yet, in the compaction stage, it was observed that, different from the other compositions, the CuPva880 feedstocks released a clear liquid when compressed, indicating that its polymeric molecules have not bound to the metallic powder as expected.

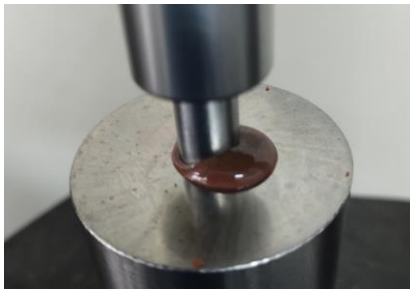

Figure 2. Copper-colored liquid released by Cu1Cmc880 cold-compaction.

2.4 3D paste extrusion

Printing tests were conducted in a 3D extrusion system that employs an extruder screw coupled to a pneumatic feeder (3D Printer Serie C, Duraprinter, Brazil) and utilizes a 0.44 mm nozzle with three translational degrees of freedom. The standard adopted design for the initial tests in this work was a cylindrical disc with 25,4 mm diameter and 5 mm height. The CAD file was designed in the software SolidWorks and the printing parameters were adjusted in the software Ultimaker Cura. The line width, corresponding to the nozzle diameter, and layer height, the distance between the nozzle and the previous layer, were both 2 mm. A 100% filling pattern was chosen. The extrusion speed was set to 33.3 mm/s and the nozzle movement speed to 3.33 mm/s. Heating was not applied, both the nozzle and the substrate operated at room temperature.

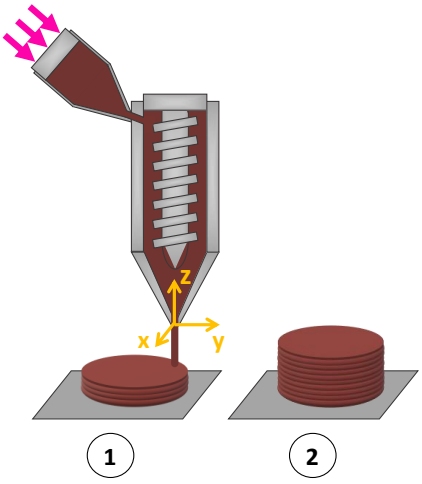

Figure 3. 3D paste extrusion method.

2.3 Thermal debinidng and sintering

The green parts went through thermal treatment in a vacuum tubular furnace. Since the copper melts at 1084.88°C, the sintering temperature should be close to 1000°C for the highest densification (Cañadilla et al., 2022). Nonetheless, at first, when the maximum programmed temperature was 930°C, it was not possible to achieve such a temperature internally because the heating program only considered the external temperature and the relation between both was still unknown. By registering the external and internal temperature over time in this first batch, it became possible to fulfill the temperature expectation for the future groups.

In the initial stage of the first try mentioned above, a heating rate of 1°C/min was applied until 300°C externally, to minimize sample deformations due to binder melting, then, the temperature was increased at a rate of 2°C/min until the debinding point, around 500°C, kept constant for 60 minutes. Next, the temperature was increased under heating of 10°C/min until it reached 880°C in the center of the furnace, which was held constant for 120 minutes to allow full

sintering. After analyzing the results of this batch, the program was updated to start heating at a rate of 2°C up to 500°C, which was held constant for 60 minutes, and then increased by 10°C/min until 1050°C externally, which resulted in approximately 980°C at the center, kept constant for 120 minutes. In both cases, after the heating was over, the dies were kept inside the furnace until they cooled down to room temperature. Treatments at higher temperatures were tested but led to deformation and an initial melting of the copper samples.

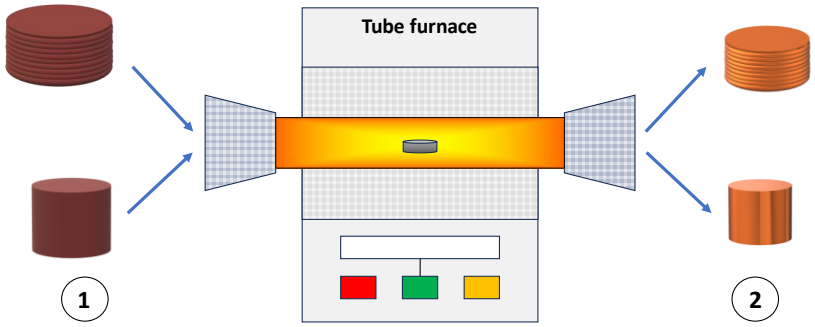

Figure 4. Thermal debinding and sintering method.

Dimensional measurements were taken before and after the thermal treatment, using a 0.05 mm-precise caliper.

2.4 Characterization

Microstructural characterization was performed in the cross-section of one polished sample of each group by using a Scanning Electron Microscope (SEM, JSM6360, Jeol, USA) and X-Ray Diffraction (XRD, D8 Bruker, Germany). The porosity was determined through image analysis on the ImageJ software, using SEM images at a 150x magnification from six distinct surface regions of each die. After, chemical etching with an Iron Chloride, Hydrochloric Acid, and Ethanol solution was applied to the die to reveal grain boundaries in optical microscopy analysis (Olympus, BX60M, Japan).

Mechanical characterization disclosed the microhardness and compressive strength. Vickers Microhardness was measured in HMV Shimadzu Microhardness tester applying a load of 980 mN for 15 s following ASTM E92-82/2003. The indentations were measured through a 40x lens. Ten measures were taken aligned with the diameter, crossing all the circular faces and giving enough space among indentations to avoid the effects of deformation. Compression tests were performed using a Universal Electromechanics Tester (DL-10000, EMIC, Brazil). Three pieces of each cold compacted group were used in the compressive strength test. The standard setup was a 0.02 mm/s speed, a 70 kN test closure load, and graphite lubrication of the surface to reduce the barreling effect.

3. RESULTS AND DISCUSSION

It was possible to observe that the sintering process resulted in the densification of the samples, leading to a linear retraction, measured along the diameter axis.

Table 2. Effects of thermal treatment in copper.

Group	Sinter Temperature, °C	Linear Retraction, %	Porosity, %
CuPva880	880	5.75 ± 0.27	13.02 ± 4.99
Cu1Cmc880	880	5.80 ± 0.27	22.34 ± 2.13
CuPvaPeg980	980	4.39 ± 3.31	2.79 ± 0.59
Cu2Cmc980	980	5.90 ± 1.39	3.13 ± 1.14
Cu2Cmc980-3D	980	19.17 ± 3.23	1.43 ± 1.22

Especially for 3D-printed parts, verifying the resulting shrinkage from the thermal treatment in paste-based copper is essential. Once the manufacturing process is based on a predefined Computer-Aided Design (CAD), over-dimensioning the project according to the predicted volumetric retraction allows the fabrication of the correct pieces. In Figure 5, it is possible to notice the high shrinkage of the 3D-extruded parts.

Figure 5. Compacted (left) and 3D extruded (right) copper samples respectively before and after thermal treatment.

The sintered parts presented a lower density than the theoretical copper density, which is expected due to the intrinsic porosity from the sintering process. The lower density can represent a desired feature for low-weight applications, such as in the aerospace field. The groups containing CMC have a higher total porosity compared to other compositions sintered at the same temperature. Noticeably, by increasing the sintering temperature from 880°C to 980°C, the porosity was considerably decreased up to 6 times in the CMC samples, according to the image analysis results. This result indicates that a higher sintering temperature is required to decrease residual porosity. Even comparing the Cu1Cmc880 and Cu2Cmc980, the effect of the temperature is more prominent than that of the CMC concentration increase.

Figure 6 shows an SEM image of samples sintered at 880˚C and 980˚C, which confirms the large difference in the porosity amount in the samples. The sample sintered at 880˚C showed an intermediary sintering stage with interconnected porosity while the samples sintered at 980˚C showed a final sintering stage with low porosity.

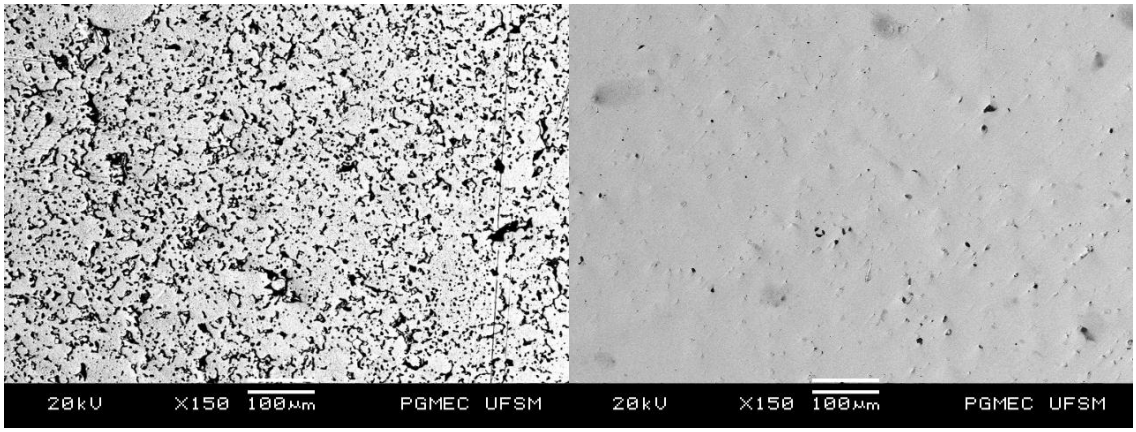

Figure 6. Scanning Electron Microscopy image of Cu1Cmc880 and Cu2Cmc980 samples, respectively.

XRD analysis was performed to verify the phase composition and possible contamination.

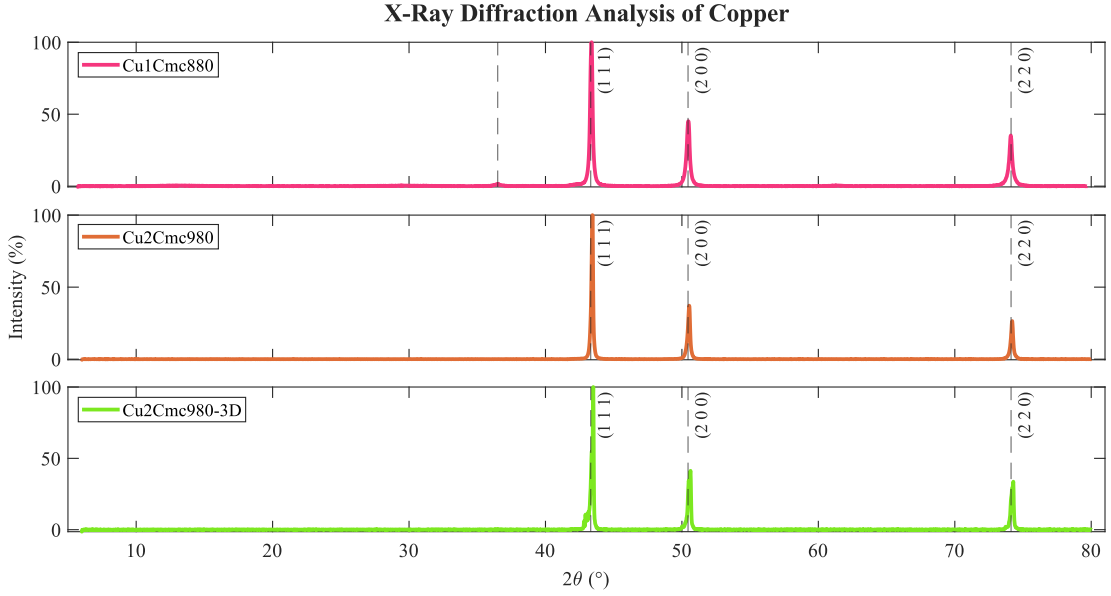

Figure 7. XRD analysis of copper samples.

The overall XRD pattern is similar for all three samples, with peaks at 2θ = 43.32°, 50.46°, and 74.12°, respectively corresponding to reflection planes (111), (200), and (220), which is in accordance with ICSD reference code 01-085-1326 for pure copper face-centered cubic crystal structure. The specimen sintered at a lower temperature unexpectedly shows a small peak at 36.50° which is probably related to SiC, used during metallography preparation of the samples.

The micrography image of the etched samples indicated that there was grain coarsening in a specific region of the sample.

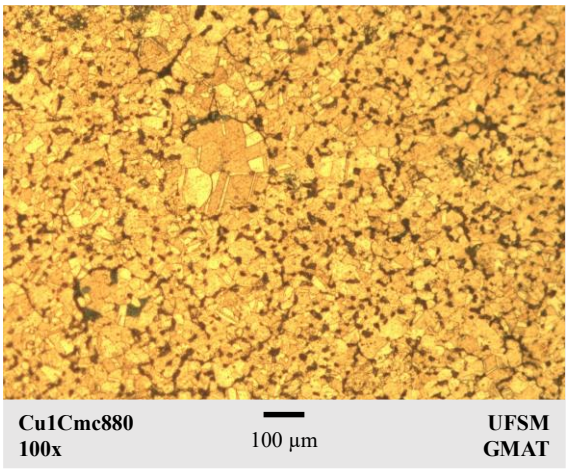

Figure 8. Micrography image of Cu1Cmc880 after etching.

Figure 9 shows the Microhardness values of copper parts. The samples sintered at a higher temperature have a slightly high hardness which can be related to the lower porosity. 3D-printed samples have a considerably higher hardness, which will be further investigated in our ongoing study.

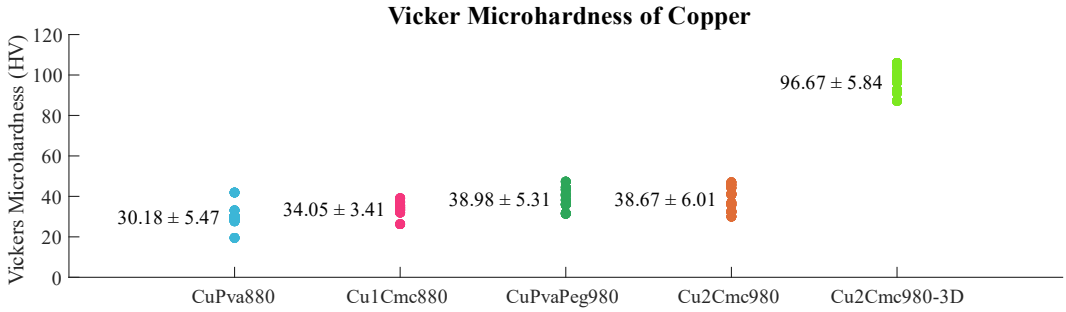

Figure 9. Vickers microhardness of copper samples.

In general, the stress-strain curves showed similar behavior in all samples, except for the group containing PVA and PEG, which failed under relatively low stress. The samples produced using CMC have slightly improved compressive strength. This behavior may be related to the oxidation of copper powders, which could have happened during oleic acid coating or due to interaction with PEG.

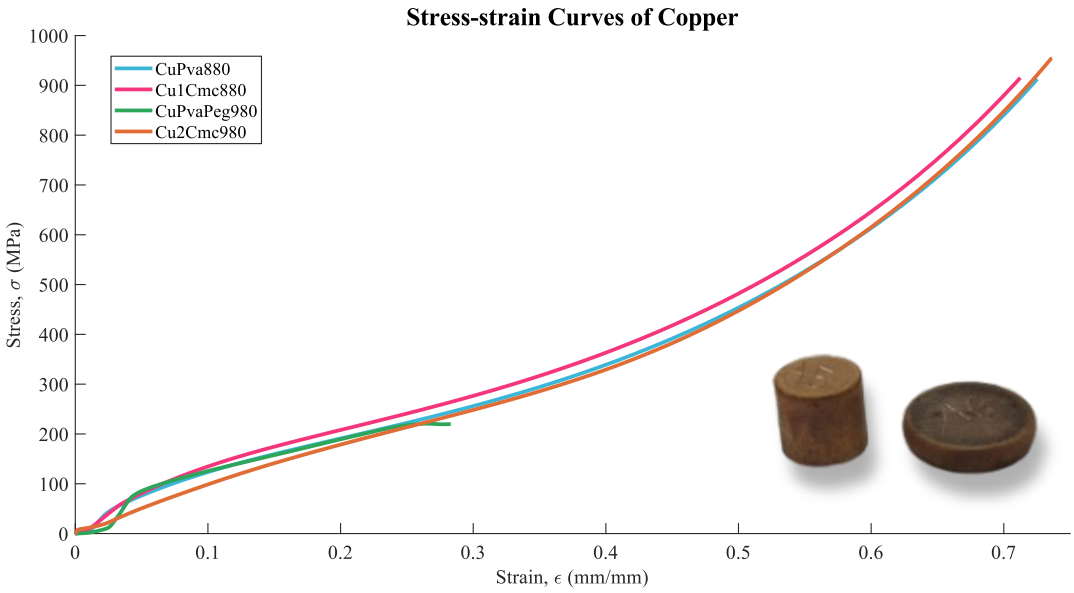

Figure 10. Stress-strain engineering curves for cold-compacted copper samples.

The compressive tests in the 3D extruded samples will be performed in our ongoing study.

4. CONCLUSIONS

In conclusion, the comprehensive exploration of the copper properties generated by highly viscous pastes has provided compelling evidence of the viability of 3D paste extrusion as a highly effective and efficient additive manufacturing method. Through this process, copper structures have been successfully manufactured. Notably, the incorporation of Carboxymethylcellulose (CMC) as a binder has demonstrated particularly promising results, yielding samples with satisfactory printability, lower porosity, higher microhardness, and higher compression strength. These attributes make the components highly desirable for demanding engineering applications like in aerospace and automotive industries, where lightweight and strong materials are in high demand. Further studies are still required to evaluate the thermal, electrical, and mechanical properties of 3D extruded samples as well as to scale up the process.

Additionally, the success of paste extrusion for copper fabrication suggests that this method has the potential to be embraced and adapted for various industrial contexts. It is expected that its affordability and feasibility will make it a suitable choice for metal prototyping, presenting a sustainable opportunity for industries to optimize their manufacturing processes while minimizing costs and environmental impact.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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