Powder-Free Fabrication of Metal and Alloy 3D Objects through Continuous Liquid Interface Production (CLIP) 3D Printing

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1. Background

Additive manufacturing (3D printing) has revolutionized the production of complex metal components, offering unparalleled precision, material efficiency, and design flexibility. However, prevalent metal additive manufacturing techniques like Laser Powder Bed Fusion (L-PBF) and Direct Energy Deposition (DED) are powder-based. These systems encounter issues such as poor surface finish, high costs, and slow printing speeds due to their layer-by-layer fabrication. This research aims to overcome these limitations by developing a powder-free, continuous metal 3D printing process. Utilizing the Continuous Liquid Interface Production (CLIP) method, dissolved metal ions are integrated directly into a water-based resin. This innovative approach eliminates powder handling, enhances light penetration, and facilitates quicker, more consistent curing.This powder-free strategy aims to enhance metal 3D printing's sustainability and scalability, with potential applications in aerospace, biomedical, and electronic manufacturing.

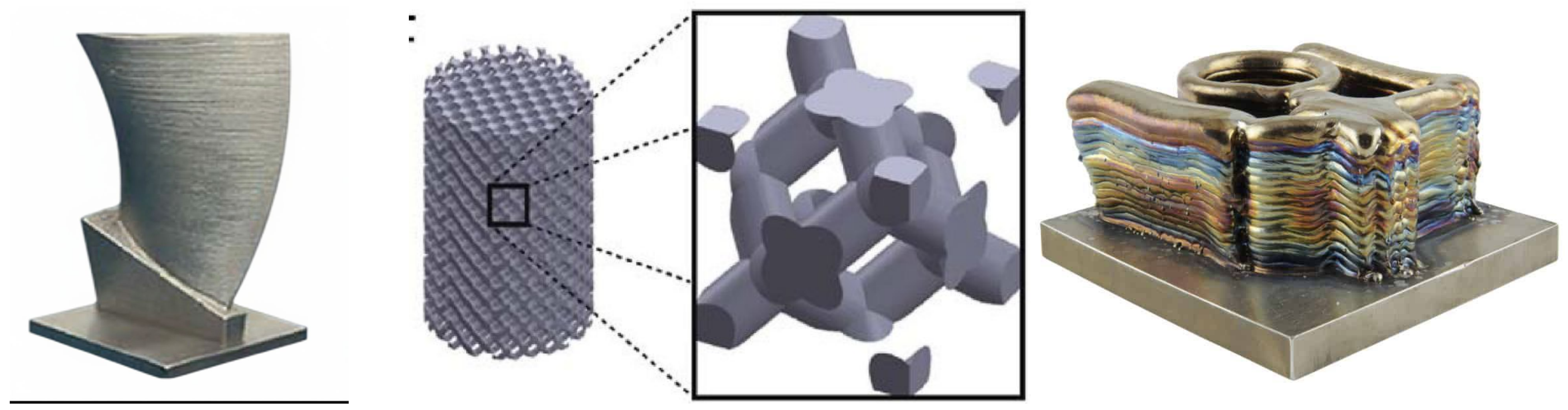

Fig 1: Laser Powder Bed Fusion (left & center), Direct Energy Deposition (right)

2. Objectives

- Develop a powder-free, water-based metal precursor resin compatible with Continuous Liquid Interface Production (CLIP) 3D printing.
- Investigate the curing behavior and self-solidification of PEGDA-based resins containing different metal salts to identify optimal formulations.
- Optimize printing parameters such as curing time and print speed to achieve continuous and uniform fabrication.
- Establish a foundation for sustainable and high-speed metal 3D printing with potential applications in aerospace, biomedical, and electronic devices.

3. Methodology

1. **Preparation of Metal Precursor Resin**

Metal Salt Solution: 75% metal salt ($AgNO_3$, $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Cr(NO_3)_3$, or $Mn(NO_3)_3$) + 25% deionized water.
Resin Solution: PEGDA (250 / 575 / 700) with 5 wt% photoinitiator (PI). Equal volumes of both solutions were mixed to obtain the printable metal-ion precursor resin.

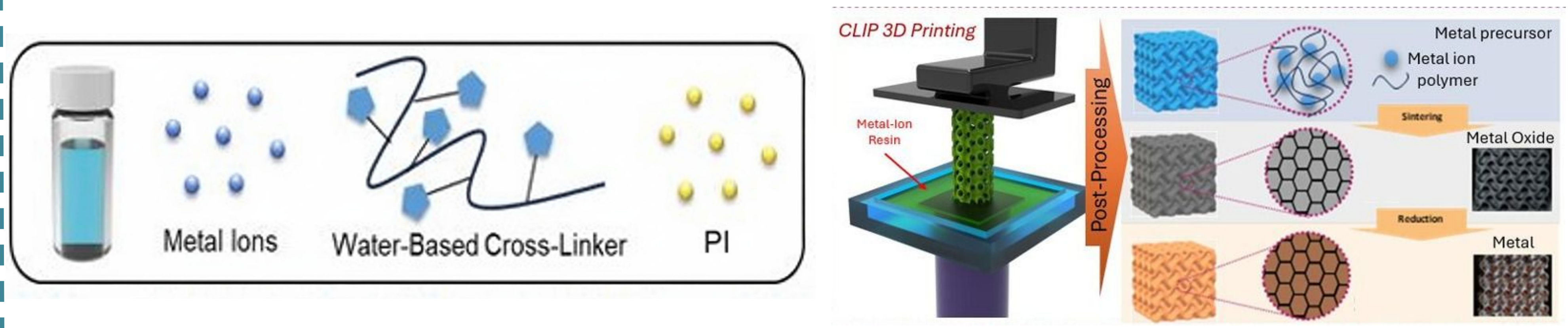

Fig 2: Powder-free metal 3D printing process overview.

2. Volumetric 3D Printing Setup

The experimental setup, shown in the figure below, is a custom-built volumetric 3D printing system designed to perform controlled curing of metal precursor resins.

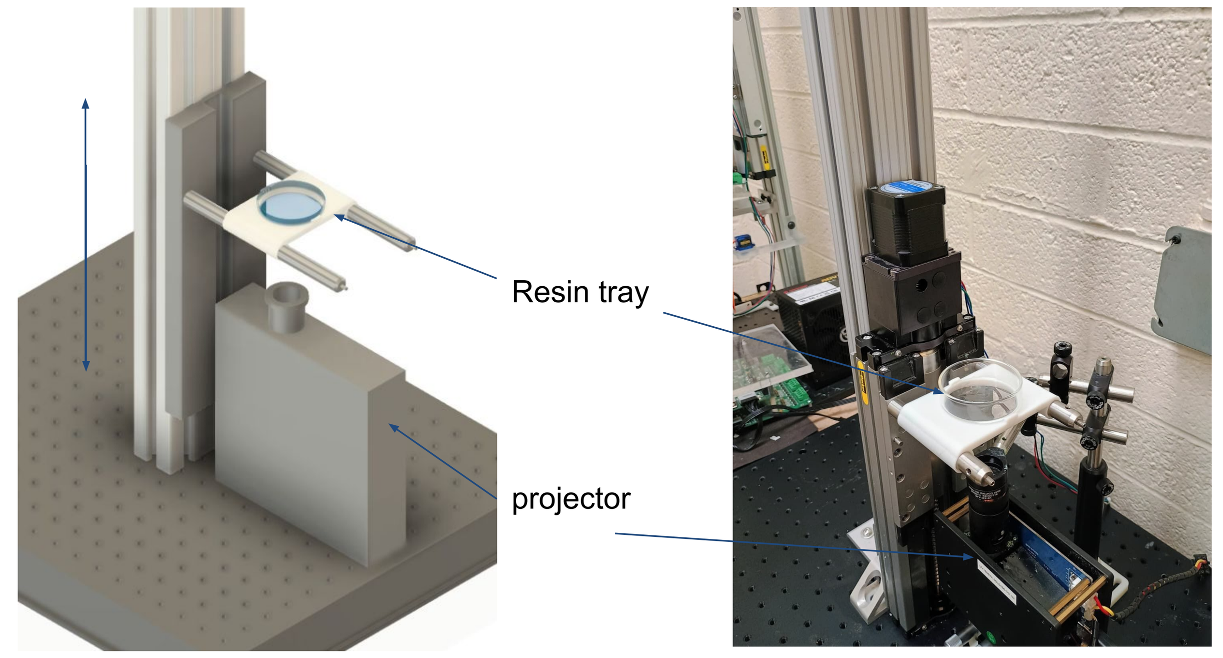

Fig 2: Volumetric 3D printer CAD model (left), & actual set up (right)

4. Optimal Dispersant Investigation

A. Self solidification test with PEG-BAPO photoinitiator :
Checking whether the system could **self-cure within 1 hour without UV exposure** using PEGDA 575 and 700 mixed with different metal salts.
Reason: To decide whether we can use those materials for our 3D printing or not.

Metal Salt	PEGDA 575	PEGDA 700
$Fe(NO_3)_3$	Solidified (~15 min)	Partial solidification (~3 hr)
$AgNO_3$	No solidification	No solidification
$Cu(NO_3)_2$	No solidification	No solidification

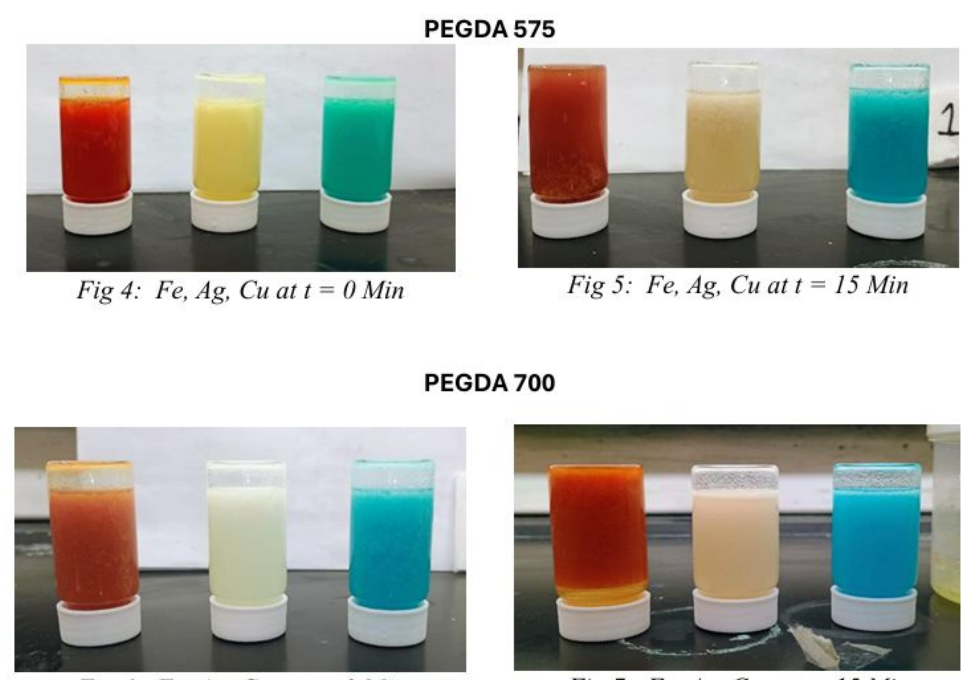

Fig 4: Fe, Ag, Cu at t = 0 Min
Fig 5: Fe, Ag, Cu at t = 15 Min
Fig 6: Fe, Ag, Cu at t = 0 Min
Fig 7: Fe, Ag, Cu at t = 15 Min

- $Fe(NO_3)_3$ self-cured without UV, making it unsuitable for UV-controlled printing.

B.Curing and Self-Solidification test with TPO Photoinitiator :
Checking whether the resins self-solidify within 1 hour (no UV) and cure under UV light (3 min exposure) for PEGDA 250, 575, and 700 with 5 % TPO.

Metal Salt	PEGDA 250		PEGDA 575		PEGDA 700	
	Self-Solidification (no UV)	UV Cured	Self-Solidification (no UV)	UV Cured	Self-Solidification (no UV)	UV Cured
$Ag(NO_3)$	No	Yes	Yes (~15 s)	N/A	Yes (~15 s)	N/A
$Cu(NO_3)_2$	No	Yes	No	Yes	No	Very less in 5 min
$Cr(NO_3)_3$	No	No	Yes (~45 min)	Yes	No	Yes
$Mn(NO_3)_3$	No	—	No	Yes	No	Yes

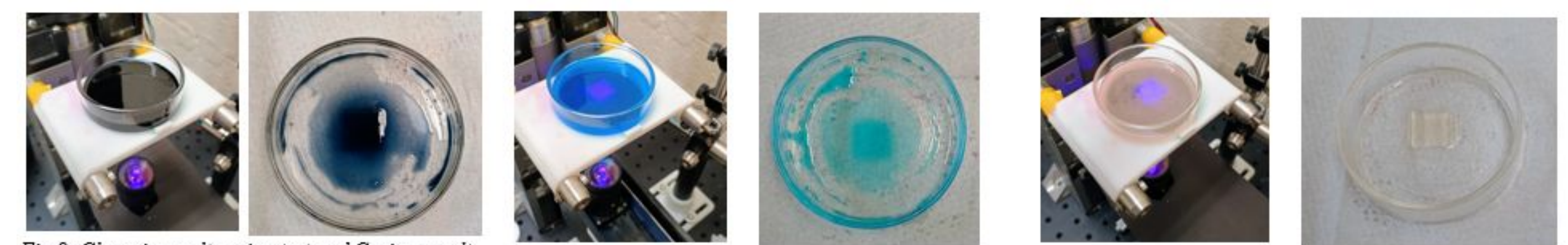

Fig 8: Chromium salt curing test and Curing result after t = 3 Mins
Fig 9: Copper salt curing test and Curing result after t = 5 Mins
Fig 10: Manganese salt curing test and Curing result after t = 3 Mins

- Curing test results of PEGDA-700 with 5% TPO photoinitiator and various metal salt solutions.

6. Future Work

Some metal ions initiate self-polymerization by generating free radicals, while others do not. The rate and nature of this behavior vary with the metal ion, PEGDA molecular weight, and photoinitiator type. Future work will optimize resin composition and exposure parameters, perform printing trials, and correlate process and material factors with the mechanical properties of printed parts.

7. Acknowledgements

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8. References

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