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Experimental Study of Localized Electrochemical Deposition using Liquid Marbles

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Abstract

A liquid marble is a droplet of liquid coated with microparticles or nanoparticles. A novel method of localized electrochemical deposition (LECD) using liquid marbles and the feasibility of application of this method in additive manufacturing/micro-repair is discussed. Controllability of the transportation of liquid marbles to any desired location by pick and place technique has been demonstrated by depositing a 3X3 grid pattern with 1mm period using an in-house built CNC setup. An experimental study was conducted to study the effect of 3 process parameters viz. duty factor, reaction time and volume of electrolyte on the height of the deposit and ANOVA was performed at 95% confidence level. It was found that the duty factor was the most significant process parameter.

Keywords: Electrochemical Additive Manufacturing, Liquid Marble, Design of Experiments

1. INTRODUCTION

The need for small parts in the micrometer range has increased tremendously in recent times. Additive manufacturing (AM) is a promising method to manufacture such small parts. While the most common materials used in additive manufacturing are thermoplastics and polymers, other engineering materials, especially metals are emerging to have a wide range of applications. Selective laser sintering (SLS) and selective laser melting (SLM) are the most common AM processes for metal additive manufacturing. Electron beam melting (EBM) and friction surfacing are relatively newer processes [2–5]. All these methods are thermal processes that involve melting of fine metal powders to different degrees and use this for creating the layers. Therefore, these processes incur thermal stresses and subsequent defect such as deformation and cracks.

To overcome the thermal effects of the conventional metal additive manufacturing processes, Localized Electrochemical Deposition (LECD) has been explored recently for micro additive manufacturing applications [6][7], wherein complex shaped micro metal parts can be fabricated without the need for support-structures. LECD uses an electrolyte tank, which consumes much more electrolyte than what is necessary and therefore, it is not cost effective in terms of consumables used. Hence a novel and eco-friendly variation of the LECD process using liquid marbles is introduced in this study.

A liquid marble is a liquid droplet coated with hydrophobic (sometimes hydrophilic) micro or nano-particles. The powder, which encapsulates the liquid, allows small quantities of liquid to be transported from one point to another without the need of micro-channels as in conventional micro fluidics. Preparation of a liquid marble is shown in Fig 1. A copper powder bed is created on a petri-dish and 2-3 μL of the liquid is measured and dropped on to the powder bed using a microliter syringe. Then the petri dish is tilted slightly and the droplet rolls and forms a liquid marble.

The liquid in this study is a nickel electrolyte (Watts bath) and using these micro reservoirs of electrolyte, localized electrochemical deposition is performed wherein copper powders were glued to the substrate with the metal from the electrolyte acting like a binding agent. The schematic for this process is shown Fig 2.

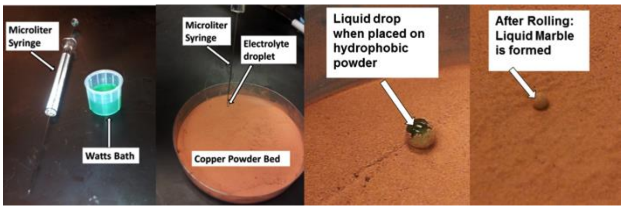

Fig 1: Preparation of Liquid Marble [8]

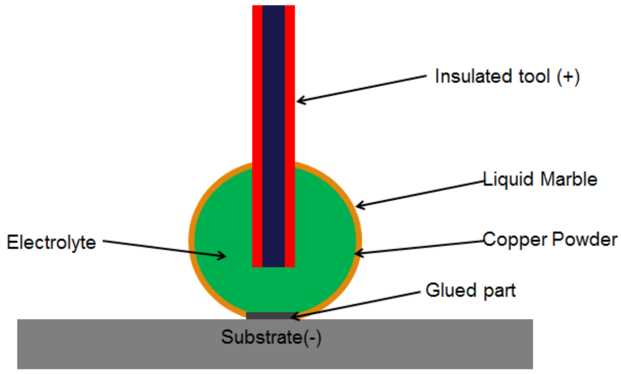

Fig 2: LECD using Liquid Marble – Process Schematic [9]

Conventionally, liquid marbles are transported using gravity, electrical, or magnetic field [10–14]. But these techniques are not precise. Pick and place technique is a precise method to manipulate the liquid marble which involves picking a liquid marble by inserting a micro tool and due to surface roughness it gets attached and then can be moved to the desired location and placed on the surface. Fig 3 demonstrates the patterning experiment and the result indicating the precise nature of pick and place method. This technique is particularly useful for target specific applications such as micro repair. The surface profiles of micro ECAM experiments for micro additive manufacturing and micro repair are shown in Fig 4 and Fig 5 [8].

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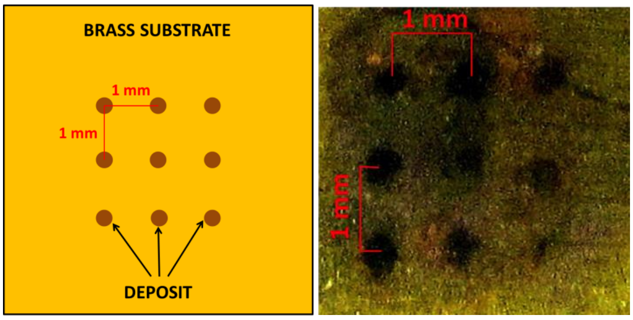

Fig 3: Controllability of Pick and Place Method [8]

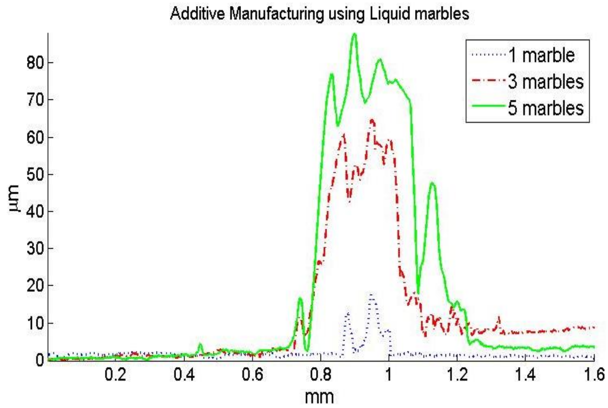

Fig 4: Additive Manufacturing Using Liquid Marbles [8]

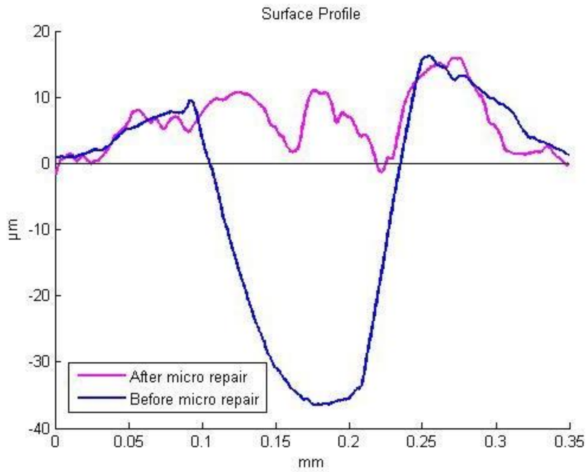

Fig 5: Micro-repair Using Liquid Marbles [8]

A mathematical model based on tool and deposit geometries to theoretically predict the height of deposition was developed and experimentally verified [9]. Corrosion study was done on the deposits and it was found that the corrosion rate of the deposit did not significantly differ from the base metal. This suggests that this process is suitable for micro-repair application [18]. An experimental study was conducted in this work to understand the effect of three process parameters viz. duty factor, reaction time and volume of electrolyte on the height of the deposit.

2. EXPERIMENTAL SETUP

A 250 µm platinum wire is used as the anode. The anode is insulated on the sides to avoid stray reactions and aid in the adhesion of the liquid marble to the anode during pick and place. A brass plate is used as the cathode. The experimental setup is shown in Fig 6.

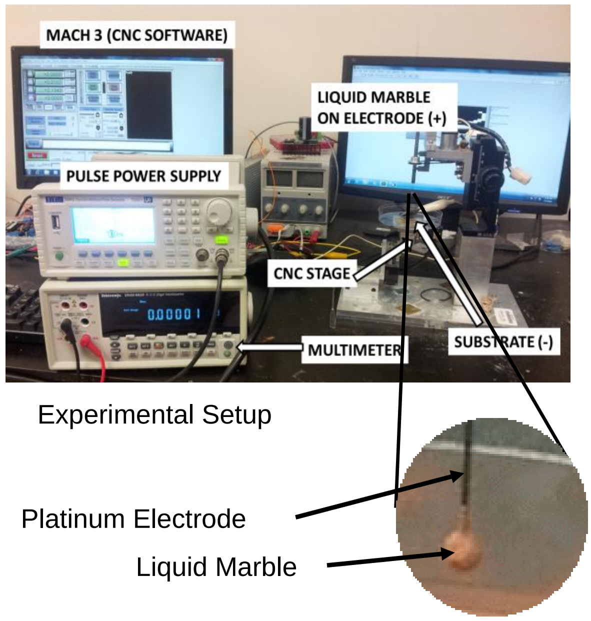

Fig 6: Experimental Setup

Mach 3 open source CNC software is used to control the CNC stage and a pulse power supply capable of producing nanosecond pulse is used as the power source. Watts bath is used as the electrolyte and its composition is given in Table 1. **The experimental conditions are shown in** Table 2.

Table 1: Electrolyte Composition [18]

Chemical	Concentration
Nickel sulfate ($NiSO_4.6H_2O$)	240g/L
Nickel chloride ($NiCl_2.6H_2O$)	45g/L
Boric acid (H_3BO_3)	30 g/L

Table 2: Experimental Conditions

Parameter	Details
Voltage	5 V
Pulse Duration	100 ns
Anode	Platinum wire ϕ250 µm
Cathode (Substrate)	Brass
Electrolyte	Watts bath

3. DESIGN OF EXPERIMENTS

Design of Experiments is a statistical method to determine the cause-effect relationship between the process parameters and the output of the process. This information can be used to modify the input parameters to optimize the output. Three control factors viz. reaction time, duty factor and the volume of the electrolyte were selected to study their effect on the height of deposition which is the output response. The control factors along with their levels are shown in

Table 3: Control Factors and Levels

Parameter	Level 1	Level 2
Reaction Time (s)	4	8
Duty factor (%)	40	70
Liquid marble size (μL)	2	4

Orthogonal arrays are constructed in a way that each level of a control factor will be matched with all the levels of other control factors equal number of times. Selection of orthogonal array depends on the number of degrees of freedom (DOF) computed for the experiments. The DOF required for 3 parameters with 2 levels each is 3 (3 X (2-1)). Since the orthogonal array chosen should be equal or greater than the DOF, L4 orthogonal array is chosen for the experiments. There were two replicate experiments for each set of factors and Table 4 shows the L4 orthogonal array. The height of deposition is determined using a surface profilometer (Mitutoya Surftest SJ-410)

Table 4: Layout of L4 Orthogonal Array

Expt No.	Reaction Time (s)	Duty Factor (%)	Volume of Electrolyte (μL)	Deposition Height (μm)
1	4	40	2	5.66
2	4	70	4	15.6
3	8	40	4	11.8
4	8	70	2	29.08

To determine the factors that significantly affect the output parameter, Minitab software was used and ANOVA was performed at 95% confidence level.

4. RESULTS AND DISCUSSION

The results for the ANOVA is shown in Table 5 at 95% confidence level. The ANOVA table shows the variation of the output parameter with respect to the contributions due to various control factors. Thus, contribution of each factor is measured having removed the effects of all other factors. The P-values and F-ratios show the statistical significance of each of the factors.

Table 5: ANOVA for Height of Deposition

Source	**Dof**	**Sum of squares**	**Mean of squares**	**F-value**	**P-value**
Reaction Time	1	182.60	182.596	31.13	0.005
Duty factor	1	348.22	348.216	59.36	0.002
Vol. of Electrolyte	1	42.78	42.781	7.29	0.054
Error	4	23.47	5.866		
Total	7	597.06			

Table 5 reveals that the P value for the volume of electrolyte is more than 0.05 at 95% confidence level which means that it is not a statistically significant factor contributing towards the height of deposition. This is due to fact that the there is still a lot of electrolyte in the liquid marble that goes unreacted in the process and therefor the volume of the actually used for the electrodeposition is almost consistent in these experiments. Duty factor has the least P value and hence is the most significant parameter. Higher the duty factor, higher the height of deposition as the duty factor determines the amount of time the current is actually used for the electrodeposition process.

Since the objective of this experiment was to determine the process parameters that give the maximum height of electrochemical deposition, the quality characteristic of 'higher the better' was chosen for statistical analysis. Table 6 shows the S/N ratios which reveals that duty factor of 70% (Level 2), reaction time of 8 seconds (Level 2) and electrolyte volume of 2 μL gives the maximum deposition height.

Table 6: S/N ratio for Height of Deposition

Factor	Level 1	Level 2
Reaction Time	20	25.34
Duty factor	18.85	26.49
Vol. of Electrolyte	22.79	22.55

5. CONCLUSION

Localized electrochemical deposition using liquid marbles is discussed in detail. Experimental study was performed with three input parameters – reaction time, duty factor and liquid marble size. Two levels were selected for each input parameter and the output parameter was the height of deposition. ANOVA was performed at 95% confidence level and it was found that the duty factor was the most significant parameter and the liquid marble size had the least effect on the height of the deposit. Information from this study can used in future studies involving LECD using liquid marbles.

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