Procedia Manufacturing
Volume 5, 2016, Pages 132–143
44th Proceedings of the North American Manufacturing Research Institution of SME http://www.sme.org/namrc

Modeling of Deposition Height in Localized Electrochemical Deposition Using Liquid Marbles

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Abstract
Application of Localized Electrochemical Deposition (LECD) using liquid marbles for micro repair and micro additive manufacturing is being researched. A liquid marble is a droplet of liquid coated with hydrophobic micro or nano powders. When a suitable electrolyte is used as the liquid, a liquid marble can be used for the LECD process. A theoretical model to predict the deposition height using a liquid marble is developed in this work. The height of deposition is a critical output parameter as it determines the minimum layer height in electrochemical additive manufacturing (ECAM). A physics based mathematical model using Faraday's law of electrolysis and the knowledge of geometry of the tool and metal powder has been developed. Experimental verification was carried out to validate the theoretical model. Experimental values follow the trend predicted by the model.

Keywords: LECD, Liquid Marbles, micro repair, additive manufacturing, process modeling

1 Introduction

Additive manufacturing (AM) is a 3D, layer-by-layer manufacturing technique, capable of producing complex 3D structure from a computer model. With the advent of product miniaturization, there is a need for complex micro parts. Micro additive manufacturing technique is now increasingly being used to produce these parts. However, the currently used micro AM technologies have several limitations ranging from material selection, porosity, internal stresses, to part strength (Vaezi et al., 2013). While most of the AM processes use thermo-plastics and polymers, there are a great number of engineering applications for metal micro parts. Powder-based metal AM processes like Electron Beam Melting and Selective Laser Sintering suffer from thermal defects (Edwards et al., 2013, Paul et al., 2014). There are other limitations such as the need for support structures, the need for powder handling systems with these AM methods. Recently a mask-less electrochemical AM technique was used to fabricate 3D micro-parts in a layer-by-layer fashion without using support structures (Sundaram et al., 2015). This technique utilizes the concept of Localized Electrochemical Deposition

 Selection and peer-review under responsibility of the Scientific Programme Committee of NAMRI/SME

doi:10.1016/j.promfg.2016.08.013

(LECD). Finite element modeling and simulations have been used to understand the effects of the process parameters ECAM (Brant et al., 2015).

ECAM by LECD uses an electrolyte bath. Using large amounts of these electrolytes is not eco-friendly and disposing of the unused materials also becomes cumbersome. Also these methods could not deposit more than one material and localization is an issue. Therefore a technique to utilize a very small amount of electrolyte (in the micro liter range) was conceptualized in an earlier work (Shailendar and Sundaram, 2014). This method uses liquid marble, a liquid droplet (electrolyte) encapsulated in a hydrophobic powder. Micro repair studies by this approach were found to have good corrosion resistance (Shailendar and Sundaram, 2015). A brief literature review on liquid marbles and LECD is given in the following section.

2 Literature Review

2.1 Liquid Marbles

Liquid marbles were first reported in 2000. They were prepared using 20 μm grain hydrophobic lycopodium powder covered with fluorinated silanes (Aussillous and Quéré, 2001). Highly hydrophilic powders like Polyvinylidene fluoride (PVDF), and even less hydrophobic powders like graphite and carbon black were also used to make liquid marbles (Bormashenko, 2011). In a study hydrophobic copper powder was used to form liquid marbles. It was found that smaller copper particles gave more stable liquid marbles (McEleney et al., 2009). Mechanism of formation of liquid marbles, static and dynamic properties, and ways to manipulate liquid marbles were studied (McEleney et al., 2009, Aussillous and Quéré, 2006, Bormashenko et al., 2010b, Bormashenko, 2011) . There are various promising applications for liquid marbles, especially in microfluidics (Zhao et al., 2010, Bormashenko et al., 2008). Liquid marbles are already being studied for potential applications like gas sensing (Tian et al., 2010), detection of pollution in water/vapor interface (Bormashenko and Musin, 2009), synthesizing solid polyelectrolyte microspheres (Bhosale and Panchagnula, 2010), rapid blood typing (Arbatan et al., 2012), optical probing (Zhao et al., 2012) and micro-pump (Bormashenko et al., 2010a).

2.2 Localized Electrochemical Deposition

Localized Electrochemical Deposition is a mask-less micro fabrication technique used to fabricate metal micro parts (Madden and Hunter, 1996, Said, 2003, Yeo et al., 2000, Seol et al., 2005). A sharp micro electrode is placed in an electroplating solution very close to a conducting substrate. When a potential is applied between the electrode and the substrate, the electric field gets localized in the region underneath the tip and hence the deposit also gets localized (Madden and Hunter, 1996).

Though the feasibility of using liquid marbles for AM and also micro repair is demonstrated in (Shailendar and Sundaram, 2014), it becomes necessary to determine the height of deposition using one liquid marble. This would enable to understand the number of liquid marbles required to deposit a particular amount of material. Therefore, a theoretical model has been developed in this work to determine the height of deposition for one liquid marble. Details of the model development is presented in the following section.

3 Process Modeling

A liquid marble is a liquid droplet encapsulated in a hydrophobic powder shell. The liquid used in this paper is Watts bath and the hydrophobic powder used is copper. It is made by taking a small quantity of the electrolyte in a micro syringe and placing the droplet on the copper powder bed in a petri dish. The petri dish is slightly tilted so that the droplet rolls over the hydrophobic powder, forming the liquid marble.

3.1 Nomenclature

The nomenclature used in the process model development is given below:

D	Diameter of the tool (µm)
d	Average diameter of Copper particle (µm)
D_a	Actual diameter of the deposit (µm)
M_{Ni}	Molar Mass of Nickel ($gmol^{-1}$)
I_{avg}	Pulsed Current (A)
t	Deposition Time (s)
n_{Ni}	Number of Valence Electrons in Nickel
F	Faraday's number
ρ_{Ni}	Density of Nickel (kg/m^3)
V_{Ni}	Volume of Nickel deposited (μm^3)
$V_{Ni/L}$	Volume of Nickel per layer (μm^3)
V_{Cu}	Volume of individual Copper particle (m^3)
$V_{Cu/L}$	Volume of Copper particles in one layer of deposition (μm^3)
k	Packing Factor
N_p	Number of Copper particles in one layer of deposit
N_L	Total number of layers of Copper on the liquid marble
N_G	Number of glued layers on the deposit
i	Iterative value where $i = 1,2,3 \ldots N_L$
h_g	Height of glued layers (Copper with Nickel binder) (µm)
V_{above}	Volume of Nickel above the glued layers (μm^3)
h_{above}	Height above the glued layers (only Nickel) (µm)
φ	Flag field (Takes value 0 or 1)
h	Height of Deposition for one liquid marble (µm)
H	Final theoretical height of the deposit (µm)

3.2 Assumptions

The following simplification assumptions were made to develop the process model. The overall approach used in the process model development is shown in Figure 1.

- The actual deposit is in the shape of a frustum. However, it is considered as a cylinder for simplification purpose. The diameter of the deposit is equal to the diameter of the tool.
- Multiple layers of copper powder are present on the liquid marble.
- Copper particles which are located under the tool only get deposited.

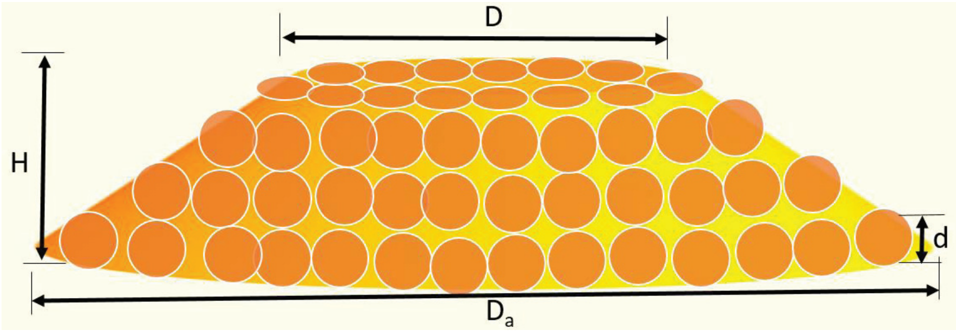

Figure 1: Schematic of actual deposit in the shape of a frustum

3.3 Development of mathematical model for the deposition height (H)

Volume of nickel per layer ($V_{Ni/L}$) can be determined from the volume of the deposit with height equal to the size of the particle and diameter equal to the diameter of the tool as

$$V_{Ni/L} = [\frac{\pi D^2 d}{4} - V_{Cu/L}] \quad (1)$$

Volume of copper in one layer ($V_{Cu/L}$) is given by the product of the volume of an individual copper particle (V_{Cu}) and number of Cu particles in one layer (N_p) as

$$V_{Cu/L} = V_{Cu} * N_p * k \quad (2)$$

where, k is the packing factor.

Number of Copper Particles in one layer (N_p) is given by

$$N_p = \frac{Cross\ Sectional\ Area\ of\ the\ Tool}{Cross\ Sectional\ Area\ of\ a\ Copper\ particle} = \frac{D^2}{d^2} \quad (3)$$

By substituting eq (3) in eq (2),

$$V_{Cu/L} = \frac{\pi D^2 d\ k}{6} \quad (4)$$

Now, substituting eq (4) in eq (1) results in

$$V_{Ni/L} = [\frac{\pi D^2 d}{4} - \frac{\pi D^2 d\ k}{6}] = \pi D^2 d\ [\frac{1}{4} - \frac{k}{6}] \quad (5)$$

Using Faraday's Law, the mass of nickel deposited can be expressed as $\frac{M_{Ni} I_{avg}\ t}{n_{Ni} F}$

Therefore, volume of nickel deposited is given by

$$V_{Ni} = \frac{M_{Ni} I_{avg}\ t}{n_{Ni} F \rho_{Ni}} \quad (6)$$

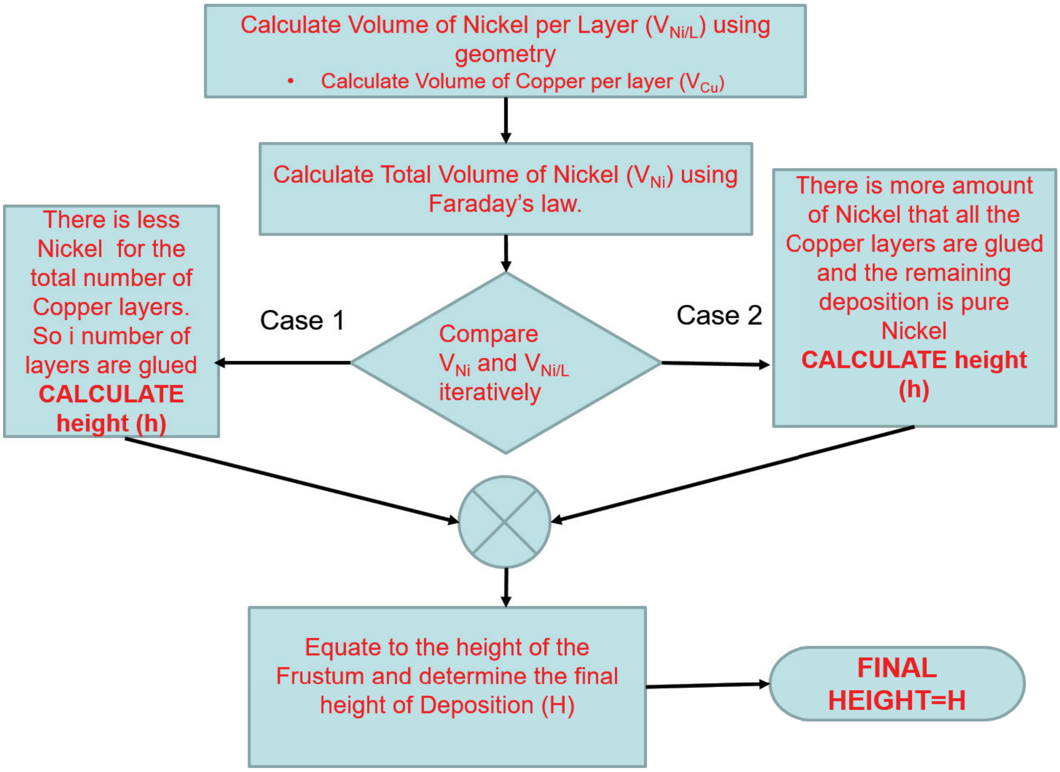

Figure 2: Flowchart for the process model

Depending on the deposition time (t) during the process, following two cases may arise:

Case 1: When the total volume of copper powder [V_{Cu} * Total number of Cu layers (N_L)] is more than the volume of nickel ($V_{Ni/L}$), the entire nickel is used to bind or 'glue' the copper powder in layers.

As the nickel from the electrolyte starts depositing on the substrate, copper powder from the liquid marbles also get deposited with nickel as the binding agent. The number of layers of copper deposited is denoted 'Glued Layers' (N_G). i is an iterative term which takes values from 1,2,3… N_L and N_G takes the value of i. This implies the maximum number of glued layers can be lesser than or equal to the number of layers of copper present on the liquid marble.

N_G = i; For, $(i-1)V_{Ni/L} < V_{Ni} < iV_{Ni/L}$ (7)

The value of V_{Ni} is checked against the volume of nickel per layer $V_{Ni/L}$ to find the number of layers glued (N_G)

The diameter of the powder (d) gives the height of one layer of deposition and hence the height of deposition for the glued layers (h_g) is given by the product of the diameter of the copper powder and the number of glued layers (N_G)

$h_{CASE\ 1} = d * N_G$ (8)'

Case 2: In this case, there is more nickel than needed to bind all the layers of copper powder and hence only nickel is deposited above the glued copper layer. In this condition $V_{Ni} > V_{Ni/L} * N_L$

V_{above} and h_{above} are the volume and height of nickel above the glued copper layers respectively.

$V_{above} = (V_{Ni} - \frac{\pi D^2 d}{4} * N_L)$
(9)

$$h_{above} = \frac{4*V_{above}}{\pi D^2} \tag{10}$$

Now height of deposition is given by adding eqn(10) to the total height of glued layers which is the product of copper powder diameter (d) and the total number of layers of copper present on the liquid marble (N_L)

$$h_{CASE\ 2} = (h_{above} + d * N_L) \tag{11}$$

Therefore, from eq(8) and eq(11) total height of deposition is given by,

$$h = \varphi h_{CASE\ 1} + (1-\varphi)\ h_{CASE\ 2}$$

$$h = \varphi * \ d * N_g + (1-\varphi)(V_{Ni} - \frac{\pi D^2 d}{4} * N_L + d * N_L) \tag{12}$$

Where,

$$\varphi = 0\ \ if\ V_{Ni} > V_{\frac{Ni}{L}} * N_L$$

$$\varphi = 1\ \ if\ V_{Ni} < V_{\frac{Ni}{L}} * N_L$$

Experimental results reveal that the diameter of the deposition spot is larger than the diameter of the tool. Therefore the shape of the deposition can be considered as a frustum with diameters D_a (diameter of the deposition spot) and D (diameter of the tool). The volume of this frustum can be equated with the volume of the cylinder with diameter D and height 'h' from eqn(12) to obtain the corrected H which is the actual height of the deposit.

Volume of a frustum is given by

$$V_{Frustum} = \frac{\pi * H}{3}\left[\left(\frac{D^2}{4} + \frac{{D_a}^2}{4} + DD_a\right)\right] \tag{13}$$

On equating the volume of frustum with the volume of cylinder the new H, which is the final theoretical height of the deposit can be obtained as

$$H = \frac{3*D^2*h}{D^2 + DD_a + {D_a}^2} \tag{14}$$

4 Experimental Work:

4.1 Estimation of number of layers in a liquid marble (N_L):

It is necessary to estimate the shell thickness and in turn determine the maximum number of layers of copper powder in the liquid marble that can be deposited. Though the mesh size of the copper powder is 325 (44 µm) the average size of the particles is much less than that. A 500 size mesh is used to reduce the size of the copper powder to less than 25 µm. For this study, highly zoomed photographs of liquid marbles of volume 2 µL was taken with a reference scale and the distances were calibrated against the reference scale using ImageJ, an open source image processing software. Then the diameters of the liquid marbles were measured and the average was calculated. The shell thickness was determined by calculating the difference between the diameter of a liquid marble and the diameter of a liquid droplet of the same volume.

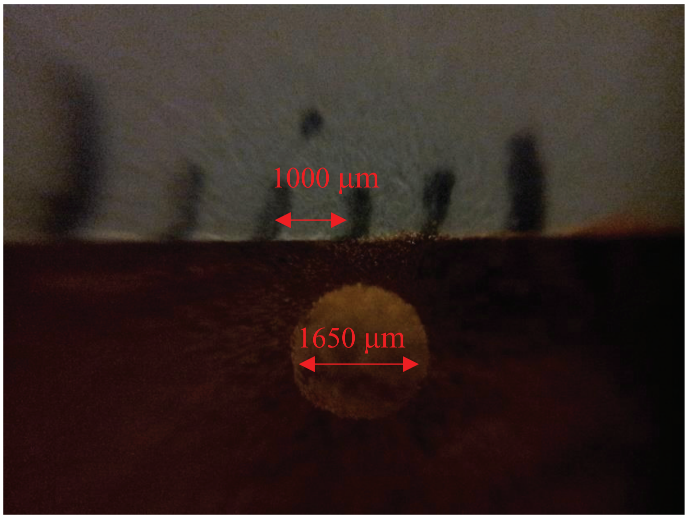

Figure 3: 2 µL Liquid marble

The average diameter of the liquid marble was found to be 1645.8 µm and hence the average shell thickness is calculated to be 41.31 µm. The average size of the particles is taken as 15 µm and so the 2 µL liquid marble is considered to be made up of about 3 layers of copper powder.

4.2 Localized Electrochemical Deposition Using Liquid Marble:

The electrolyte used for the LECD process is Watts bath. Its composition is given in Table 1.

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 1: Composition of Watts Bath

A 500 size mesh is used to reduce the size of the copper powder to less than 25 µm. The liquid marble is prepared by taking 2 µL of the electrolyte in a micro syringe and placing the droplet on a petri dish containing hydrophobic copper powder. When the petri dish is slightly tilted the copper powder gets coated on the electrolyte droplet forming a liquid marble.

A slender micro tool of diameter 250 µm, coated with enamel, is inserted inside the liquid marble and due to the difference in hydrophobicity and surface area, the liquid droplet gets 'picked' by the micro tool. Then it is placed over a substrate for the electrochemical deposition process.

The schematic for the LECD using liquid marbles is shown in Figure 4 and the experimental set-up for the same is shown in Figure 4.

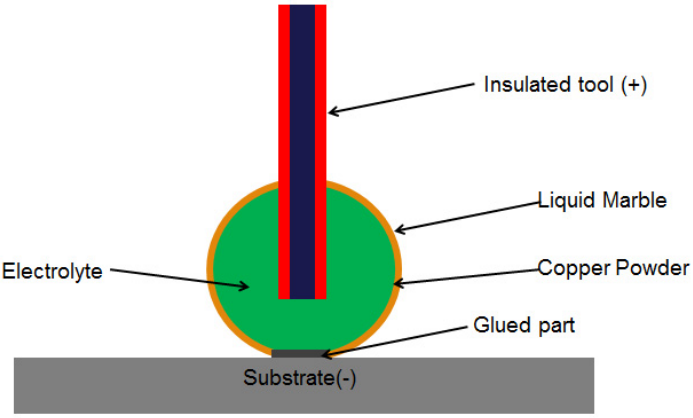

Figure 4: Schematic for LECD using Liquid Marble

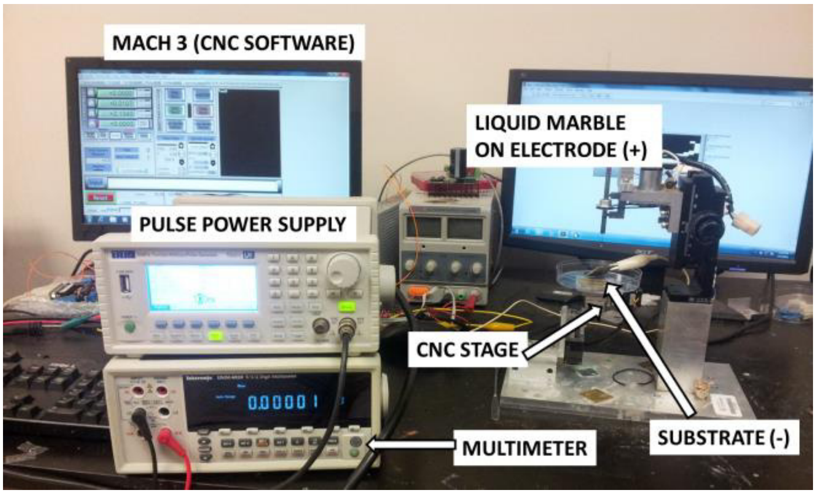

Figure 5: Experimental Setup for LECD using Liquid Marble

4.2.1. Determination the Diameter of Deposition (D_a):

The reaction time was kept a constant at 5 s and the LECD process was carried out using a 2 μL liquid marble. The experimental conditions are listed in the table below.

Parameter	Details
Voltage	5 V
Pulse Duration	100 ns
Duty Factor	50%
Anode	Platinum rod coated with enamel ϕ250 μm
Cathode (Substrate)	Brass
Electrolyte	Watts bath
Electrolyte Volume	2 μL
Reaction Time	5 s

Table 2: Experimental Conditions for D’ calculation

An optical microscope is used to measure the diameter of the deposit and the average is taken (Figure 6). The average diameter of the deposition spot is found to be 649.73 µm.

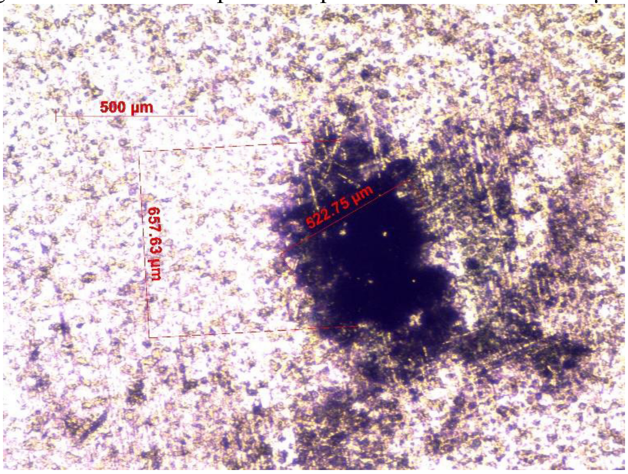

Figure 6: Diameter of the Deposit

4.2.2. Localized Electrochemical Deposition Experiments to Determine the Height of Deposition (H):

The experimental conditions are provided in the following table.

Parameter	Details
Voltage	5 V
Pulse Duration	100 ns
Anode	Platinum wire coated with enamel ϕ250 µm
Cathode (Substrate)	Brass
Electrolyte	Watts bath
Electrolyte Volume	2 µL

Table 3 Experimental Conditions

Time is kept as a variable and the experiment is carried out for 2 s, 6 s and 8 s. The deposited spots are cleaned using acetone and then the heights of deposition are measured using a surface profilometer (Mitutoyo Surftest SJ 410) and the results are presented in Table 4. The experimental error is shown in Figure 7.

Time (s)	Experimental Height(µm)
2	4.87
4	7.76
6	8.84

Table 4: Experimental Height of Deposition

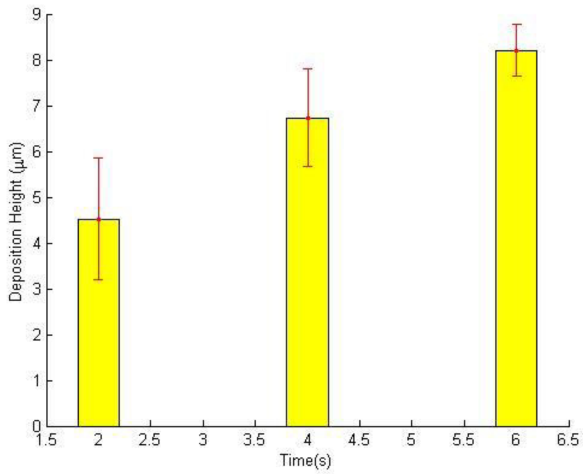

Figure 7: Experimental error for reaction times 2s, 4s and 6s.

5 Process Model Validation

The theoretical height of deposition is obtained using the mathematical model explained in Section 4. The calculation data to estimate the theoretical values of the depositions height is given Table 5. This theoretical height of deposition is compared with the experimental data in Figure 8. It can be seen that for a reaction time of 2 s, the experimental and theoretical values match very well, whereas for higher reaction times, the theoretical model over predicts the value of deposition height, possibly due to the simplifications assumptions in the model development.

Parameter	Symbol	Value	Unit
Tool Diameter	D	250	μm
Average Size of Copper Particle	d	8	μm
Mean Current	I_{avg}	0.0045	A
Molar Mass of Nickel	M_{Ni}	58.6934	$gmol^{-1}$
Density of Nickel	ρ_{Ni}	8908	kgm^{-3}
Number of Valence Electrons in Nickel	n_{Ni}	2	No Unit
Faraday's Number	F	96500	$Cmol^{-1}$
Actual Diameter of the Deposit	D_a	650	μm

Table 5: Calculation data for the estimation of deposition height

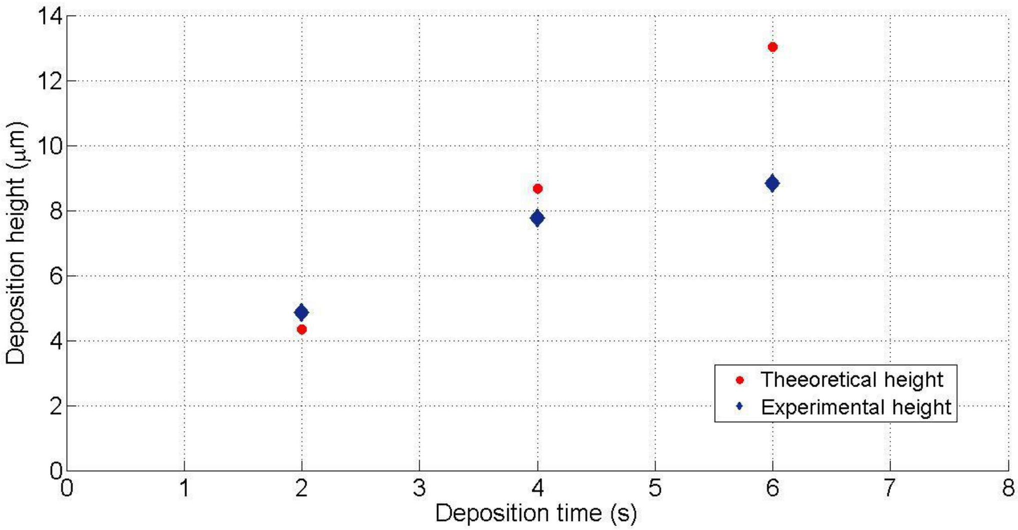

Figure 8 Comparison between experimental height and theoretical height of deposition for reaction times 2s, 4s and 6 s

6 Conclusion

A theoretical model to predict the deposition height using a liquid marble is developed in this work. The height of deposition is a critical output parameter as it determines the minimum layer height in electrochemical additive manufacturing (ECAM). A physics based mathematical model using Faraday's law of electrolysis and the knowledge of geometry of the tool and metal powder has been developed. Experimental verification was carried out to validate the theoretical model. Experimental values follow the trend predicted by the model. Therefore this theoretical model can be used to determine the number of liquid marbles that would be required to deposit a given height of material for micro repair and micro additive manufacturing applications.

Acknowledgement

Financial support provided by the National Science Foundation under Grant Nos. CMMI-1400800, and CMMI-1454181 is acknowledged.

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