

Thermal Energy Analysis for Sulfuric Acid Dilution Step in Copper Electroplating Process

Chamaimon Boonrit and Satok Chaikunchuensakun

Energy and Environment Technology Management, Department of Chemical Engineering,
Faculty of Engineering, Thammasat University,
Khleng Luang, Pathumthani, Thailand, 12120
E-mail: csatok@engr.tu.ac.th

Abstract

In the pre-treatment step of copper electroplating process, sulfuric acid diluted to 5-12% by volume solution is used as a solvent to remove contaminants from the product prior to the electroplating process. Because of heat of solution, the solution temperature increases. However, electroplating process begins only when the diluted sulfuric solution reaches the set temperature. At present, there is no tool to predict this set time at a specific temperature resulting in difficulty in operation. The developed mathematical model accounts for two modes of heat transfer; conduction and convection at the surface of the mixing bath. The results show that the developed model could well predict the setting time with an average error of less than 7.57 minutes and predict the maximum temperature with an average error less than 6.04 °F.

Keywords: heat of dilution, heat of conduction, heat of convection, overall heat transfer coefficient, polynomial equation,

1. Introduction

In the copper electroplating process, direct electric current is used to plate copper onto the surface of a product. The treatment step is the process for removing contaminants by using sulfuric solution as a cleaning solvent prior to the plating step. Sulfuric solution is used for pretreatment in four mixing baths, each of which has a different concentration depending on purpose of use, namely; acid cleaner (for cleaning oil and finger prints), acid rinsing (for cleaning copper oxide), micro etching (to etch the copper layer) and stripping (for cleaning and etching copper deposited).

In the dilution process of sulfuric acid, a lot of heat is generated thus increasing temperature of the solution in each bath. However, the later step,

electroplating process, begins when the temperature of the solution reaches the set temperature, resulting in waiting time. This waiting time is varies depending on concentration of sulfuric acid, material of the bath, cooling and heating system and environment condition. The objective of this work is to develop a mathematical model to predict the waiting time, set up time.

2. Experimental

2.1 Experimental Data

Materials of baths were; polypropylene with thickness (Δx) of 1 cm, PVC with thickness (Δx) of 1 cm and glass epoxy with thickness (Δx) of 0.8 cm.

The room temperature maintained at 77 ± 5 °F) with a relative humidity of 74

$\pm 10\%$. The dilute solution temperature of each bath was measured by thermocouple (type K) with the accuracy of $\pm 5^\circ\text{F}$.

Making the dilute solution was as follows:

1. Clean bath and add De-ionizer water to two thirds full in each bath
2. Supply 89% by volume sulfuric acid (Commercial grade) into each batch for 7, 9, 11 and 12 % by volume.
3. Turn on the circulating pump, cooling and heating system and wait for temperature to decrease to set temperature then add other chemicals.

2.2 Development of Mathematical Model

2.2.1 Heat of Dilution

Enthalpy of sulfuric solution is fitted with a polynomial equation from enthalpy concentration diagram [1]

$$H(T) = a + bx + cx^2 + dx^3 + ex^4 \quad (1)$$

where

$$a = -35750 + 11954 T - \frac{2080}{10^3} T^2 + \frac{6558}{10^6} T^3 \quad (2)$$

$$b = -5.042 + 0.090T - 0.1752T^2 + \frac{1.200}{10^6} T^3 \quad (3)$$

$$c = 0.150 - \frac{6.637}{10^3} T + \frac{1.210}{10^4} T^2 - \frac{8.150}{10^7} T^3 \quad (4)$$

$$d = -\frac{2.645}{10^3} + \frac{1.188}{10^4} T - \frac{2.138}{10^6} T^2 + \frac{1.447}{10^8} T^3 \quad (5)$$

$$e = \frac{1.877}{10^5} - \frac{7.420}{10^7} T + \frac{1.328}{10^8} T^2 - \frac{9.015}{10^{11}} T^3 \quad (6)$$

And x is mass fraction of sulfuric acid. This evaluation is for temperature range 32-212 °F.

2.2.2 Model Equation

Two heat transfer models were developed in this work. The first model was applied for baths 1 and 3 and the second model applied for baths 2 and 4.

Model 1: No cooling system

Energy balance:

Accumulated energy = Energy in – Energy out

Then

$$(M_1 + M_2) \frac{dH}{dt} = - \sum_i U_i A_i (T - T_a) \quad (7)$$

Integration of equation (7) will give a result as follows

$$t_f = - \frac{M_1 + M_2}{UA} \left[K_0 \ln(T - T_a) + K_1 T + K_2 T^2 + K_3 T^3 - C \right] \quad (8)$$

Where

M_1, M_2 are weight of water, sulfuric acid respectively

$$K_0 = b + 2cT_a + 3dT_a^2 + 4eT_a^3 \quad (9)$$

$$K_1 = 2c + 3dT_a + 4eT_a^2 \quad (10)$$

$$K_2 = (3d + 4eT_a) / 2 \quad (11)$$

$$K_3 = 4e / 3 \quad (12)$$

$$C = \frac{(M_1 H_{(0\% @ 30^\circ\text{C})} + M_2 H_{(x\% @ 21^\circ\text{C})})}{(M_1 + M_2)} \quad (13)$$

Model 2: With cooling system

Baths 2 and 4 were cooled by cooling water, therefore the energy balance equation can be written as equation (14) where CL is the cooling rate.

Energy balance:

Accumulated energy = Energy in – Energy out
Then

$$(M_1 + M_2) \frac{dH}{dt} = - \sum_i U_i A_i (T - T_a) - CL \quad (14)$$

Integration of equation (7) will give a result as follows

$$t_f = -(M_1 + M_2) \left[K_0 \ln R + K_1 R + K_2 \frac{R^2}{2} - C \right] \quad (15)$$

where

M_1, M_2 are weight of water, sulfuric acid respectively

$$K_0 = \left[\frac{b}{UA} + \frac{2c}{(UA)^2} (UAT_a - CL) + \frac{3d}{(UA)^3} (UAT_a - CL)^2 + \frac{4e}{(UA)^4} (UAT_a - CL)^3 \right] \quad (16)$$

$$K_1 = \frac{1}{(UA)^2} \left[2c + \frac{6d}{(UA)^2} (UAT_a - CL) + \frac{12e}{(UA)^4} (UAT_a - CL)^2 \right] \quad (17)$$

$$K_2 = \frac{3d}{(UA)^3} + \frac{12e}{(UA)^4} (UAT_a - CL) \quad (18)$$

$$R = UA(T - T_a) + CL \quad (19)$$

Where R is Resultand heat Transfer rate

2.2.3 Parameter Estimation

Overall Heat Transfer Coefficient; U [2]

$$U = \frac{1}{\frac{1}{h} + \frac{\Delta x}{k}} \quad (20)$$

where

k is thermal heat transfer coefficient. h is heat of convection coefficient.

Thermal heat transfer coefficient:

PP = 0.07 Btu/hr ft °F,

PVC= 0.22 Btu/hr ft °F,

Glass epoxy= 0.23 Btu/hr ft °F.

In this evaluation, heat convection was free convection; therefore h can be calculated from the equation below

Free convection at a vertical wall [3]

$$\frac{hL}{k_f} = Nu = 0.825 + \frac{0.670 \cdot Ra_f^{\frac{1}{4}}}{[1 + (0.492/Pr_f)^{\frac{9}{16}}]^{\frac{4}{9}}} \quad (21)$$

for $0 < Ra_f < 10^9$, $0 < Pr_f < \infty$

Free convection at a horizontal plate:
Heated plate facing upward or cooled plate facing downward:

Top cover of the bath:

$$h = 0.233 \left(\frac{\Delta T}{L} \right)^{\frac{1}{4}} \quad (22)$$

Heated plate facing downward or cooled plate facing upward [4]:

Bottom of the bath:

$$h = 0.104 \left(\frac{\Delta T}{L} \right)^{\frac{1}{4}} \quad (23)$$

The overall heat transfer coefficients of each bath are shown in table 1.

Table 1 Summary data of overall heat transfer coefficients

Bath (bottom)	UA (Btu/min °F)	U (cover) (Btu/min ft² °F)	U (wall) (Btu/min ft² °F)	U (Btu/min ft² °F)
1	188	6.5	2	10
2	200	2.9	3.5	16
3	173	6.5	2	10
4	200	2.9	3.5	16

Note that the overall heat transfer coefficient (U) is assumed to be constant since the process is operated under a narrow range of temperature 80-150 °F

3. Results and Discussions

3.1 Bath 1: Sulfuric acid was diluted to a concentration of 11.0 % by volume. Baths were made from PP and glass epoxy with surface area of 53.82 ft². Heat of dilution generated was 52.8 Btu/lb. When this data was applied to equation 15, it gave a relationship between t_f and T as shown in Figure 1

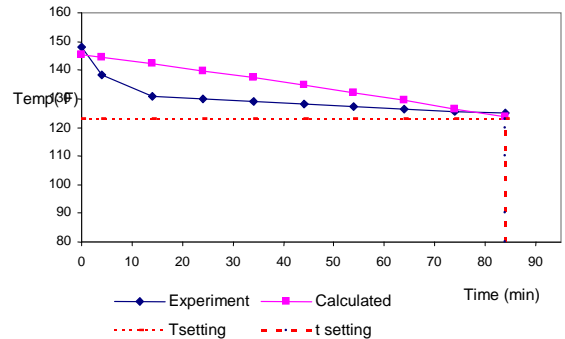


Fig.1 Temperature Profile of Sulfuric Solution at Bath 1.

In this bath, the setting temperature was 123°F. When temperature in bath reduced to near the set temperature T_{sp} , the heater (power 4 watt, 3 pcs) was started to maintain and control T_{sp} . So this evaluation model for find t_f , calculated time until T_{sp} . From the graph, t_f calculated was 80.05 minutes and T_{max} calculated was 145.47°F.

3.2 Bath 2: Dilute sulfuric acid of concentration 6.9 % volume. Bath made from PP with surface area of 36.73 ft². Heat of dilution generated was 53.54 Btu/lb. When this data was used in equation 8, it gave a relationship between t_f and T as Figure 2.

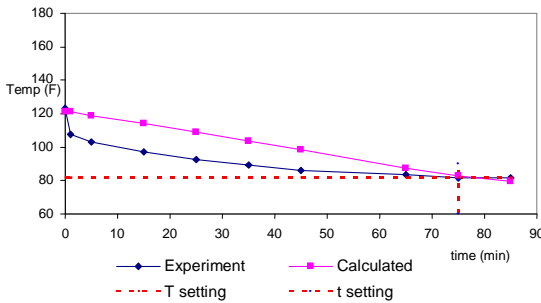


Fig.2 Temperature Profile of Sulfuric Solution at Bath 2.

In this bath, the set temperature was 81.5°F. T_{sp} was nearly ambient temperature. Therefore this bath had to have a cooling system to maintain T_{sp} with cooling rate 1.74 Btu/minute. Figure 2 shows that t_f calculated was 69.16 minutes and T_{max} calculated was 121.44°F.

3.3 Bath 3: Contained dilute sulfuric acid of concentration 11.0 % volume. The bath was made from PP and surface area was 51.13 ft². Heat of dilution generated was 52.58 Btu/lb. When this data was used in equation 8, it resulted in the relationship between t_f and T as shown in Figure 3.

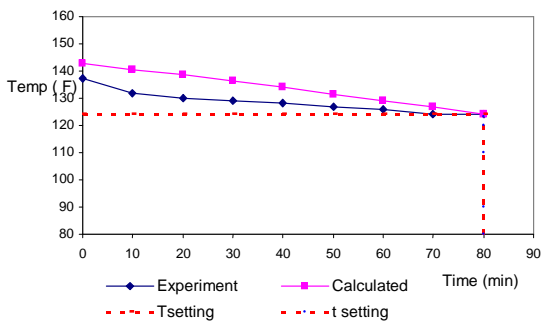


Fig.3 Temperature Profile of Sulfuric Solution at Bath 3.

In this bath, the set temperature was 123.9°F.

Bath 3 prevented temperature decline by the same method as for Bath 1 because the materials of the bath and structure were the same. So the

mechanism of heat transfer was the same. T_{max} on Bath 1 was higher than Bath 2 because the bath side and the amount of sulfuric acid filled in Bath 1 were more than Bath 2 at the same % concentration.

From the graph shown, t_f calculated was 81.14 minutes and T_{max} calculated was 142.78°F.

3.4 Bath 4: Dilute sulfuric had a concentration of 8.0 % volume. The bath was made from PP and glass epoxy with surface area of 88.39 ft². Heat of dilution generated was 53.18 Btu/lb when this data was applied to equation 15, it gave a relationship between t_f and T as shown in Figure 4.

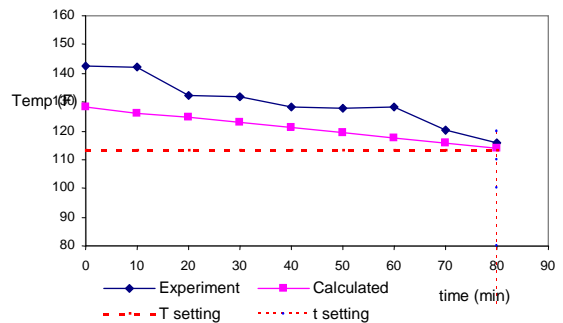


Fig.4: Temperature Profile of Sulfuric Solution at Bath 4.

In this bath, the set temperature was 115.8° F. The bath had a big volume and a cooling system to reduce waiting time with cooling rate of 2.85 Btu/minute. From the graph shown, t_f calculated was 70 minutes and T_{max} calculated was 128.3°F.

Table 2 summary data from experiment and calculate of each bath

Bath	1	2	3	4
Average				
ΔT_{max}	2.39	2.09	-5.37	14.32
6.04				
Δt_f	4.38	-5.16	-10.74	10.01
7.57				

From Table 2, the model of calculated ΔT_{\max} (T_{\max} calculated - T_{\max} of experiment) was not very different, average error 6.04°F and Δt_f (t_f calculated - t_f of experiment) was also not very different, average error 7.57 minutes. The problem was only Bath 4 that had a big volume. The error came from unsteady mixing.

However, in real practice, it is recommended to prepare a solution 10 minutes prior to the calculated heating time.

4. Conclusion

Two heat transfer models, a non-cooling system and a cooling system, were developed in this work for predicting the set time in the sulfuric dilution process. The developed models can accurately predict the set times for all baths with errors less than 10 minutes. However, for a non-cooling system and cooling system in a large bath, larger deviations between experimental and simulation data are seen at early stages of the dilution process due to unsteady-state and non perfect mixing.

5. Acknowledgement

All experiment work was supported by PCTT Company,

6. Nomenclatures

x	mass fraction
M_1, M_2	weight (lb)
h	heat convection coefficient (Btu/hr ft ² °F)

K	thermal conduction coefficient (Btu/hr ft °F)
U, U_i	Overall heat transfer coefficient (BTU/min)
A, A_i	Area (Ft ²)
H	Enthapy (Btu/lb)
T	Temperature (°F) at all equation
T_a	Ambient temperature (°F)
$Ra=(GePr)$	Rayleigh number
Nu	Nusselt number
Pr	Prandtl number
Ge	Grashof number
L	length (ft)
t	time (min)
t_f	setting time (min)
T_{sp}	Temperature setting (°F)
CL	Cooling rate (Btu/min)

7. References

- [1] Robert H., Perry Don, W. Green., Perry's Chemical Engineers' Handbook, McGraw-hill International Editions, pp. 2-185, 2-303.
- [2] W. L. McCabe, J.C. Smith, P. Harriott., Unit Operations of Chemical Engineering, McGraw-hill, pp. 285-373, 1993.
- [3] J. Sucec., Heat Transfer, Wm. C. Brown Publishers, pp. 1-266, 612-671, 1985.
- [4] J. P. Holman., Heat Transfer, McGraw-hill, pp. 336-390, 1997.