Measurement of the Cupric Ion Concentration Variation near Electrodes in the Copper Electroplating System

Je-Young Moon and Bum-Jin Chung*
Department of Nuclear Engineering, Kyung Hee University
#1732 Deokyoung-daero, Giheung-gu, Yongin-si, Gyeonggi-do, 17104, Korea
**Corresponding author: bjchung@khu.ac.kr*

1. Introduction

In-Vessel Retention - External Reactor Vessel Cooling (IVR-ERVC) of core melt is one of the key severe accident management strategies. The metallic layer is heated from below by the decay heat generated at the oxide pool, and is cooled from top and side walls (Fig. 1). The heat fluxes to the side wall imposed at the upper metallic layer, are known to increase with the reduction of layer height. This "Focusing effect" is varied by cooling condition of upper boundary and height of the metallic layer [1~3].

The experimental study for the focusing effect was carried out previously [4]. The heat transfer experiments were replaced by mass transfer experiments based on the heat and mass transfer analogy concept.

When the electroplating system is adopted as the mass transfer system, in order to simulate the different temperature conditions of top and side walls, an electrical resistance was attached to the top wall so that it is mimics hotter wall condition. Because the quantitative temperature conditions according to the electrical resistance were unknown, the methodology development is necessary.

This study investigates the methods of concentration measurement: RGB (Red, Green and Blue), Brightness, ICP (Inductively Coupled Plasma), PIV (Particle Image Velocity), and Interferometry.

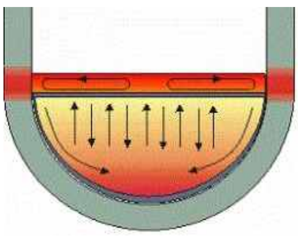


Fig. 1 Distribution of relocated molten core material.

2. Experimental Methodology

Heat and mass transfer systems are analogous, as they are described by the same mathematical formulations with the same class of boundary conditions [5]. A copper sulfate-sulfuric acid ($CuSO_4$-H_2SO_4) electroplating system was adopted as the mass transfer system. The transfer of cupric ions from the copper anode to the cathode submerged in an aqueous solution of sulfuric acid and copper sulfate is analogous to the transfer of heat. Further details of this methodology can be found in Chung et al. [6, 7].

In electroplating systems, the mass transfer coefficient is calculated based on the measured electric current and the difference in the cupric ion concentration. Through the concentration change in the mass transfer, the temperature conditions wall be revealed. As it is difficult to measure the cupric ion concentration at the cathode surface, the methodology development is necessary. In order to measure the cupric ion concentration in the copper plate, this study investigates the method of concentration measurement: RGB (Red, Green and Blue), Brightness, ICP (Inductively Coupled Plasma), PIV (Particle Image Velocity), and Interferometry.

3. Methodology Development

3.1 Apparatus and test matrix

Figure 2 shows the test rig for the measurement of cupric ion concentration. The test section is a rectangular tank made of acryl. In order to minimize the refraction of light, the thickness of acryl is 0.005 m. According to analogy concept of heat and mass transfer, each side wall simulates heated wall and cooled wall. The vertical plate was used in order to establish a known, the simple geometry.

The test matrix shown in Table I. The Rayleigh number ranged from 1.06×10^{10} to 2.87×10^{11}. The mass transfer experiments were performed using a copper sulfate-sulfuric acid ($CuSO_4$-H_2SO_4) electroplating system.

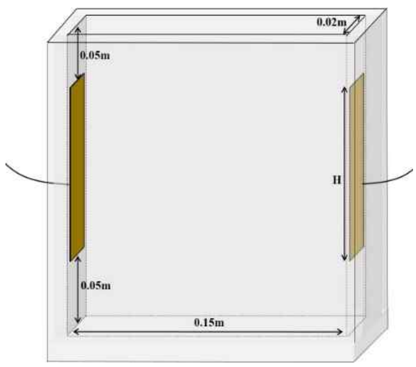


Fig. 2. The test rig for concentration measurement.

Table I: Test matrix for concentration measurement

Pr	*W*(m)	*H*(m)	Ra_H
2,014	0.02	0.05	1.06×10^{10}
		0.10	8.49×10^{10}
		0.15	2.87×10^{11}

3.2 RGB Method

RGB (Red, Green and Blue) refers to a system for representing the colors to be used on a display. Red, green and blue can be combined in various proportions to obtain any color in the visible spectrum. The red, green and blue light are combined to make millions of colors [8].

In order to confirm the variation of the cupric ion concentration using RGB method, the images of the concentration boundary layer are needed. In this work, the concentration boundary layer in the mass transfer corresponds to the thermal boundary layer in the heat transfer. As Prandtl number is very high in this study, the thickness of the concentration boundary layer becomes smaller about 2.0×10^{-4} m. So an optical microscope was used to obtain a high-magnification and high-resolution image. Fig. 3 presents the test image of middle position for the height of 0.015m. As soon as the voltage was applied, the transparent layer was formed by concentration change of the cupric ion. Brightness and PIV method are similar to this imaging process.

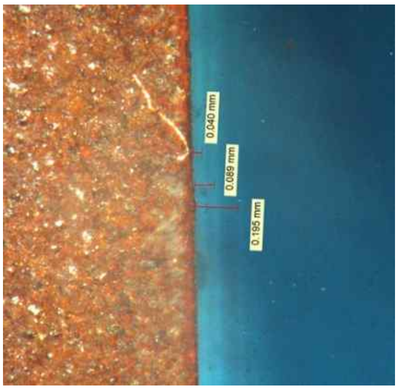


Fig. 3. The test image using the optical microscope.

3.3 ICP Method

An Inductively Coupled Plasma (ICP) can be generated by directing the energy of a radio frequency generator into a suitable gas, usually ICP argon. Other plasma gases were used such as Helium and Nitrogen. ICP can be very powerful tools for detecting and analyzing trace elements [9].

In order to analyze the cupric ion concentration using ICP method, the solution samples were taken from the electrode surface. The process is as follows: (a) 1 – 10 μl of the solution is taken using micro pipet due to the thin concentration boundary layer, (b) the sample was diluted with distilled water because the minimum quantity of ICP test sample is 10 ml, (c) after the preprocessing, the analysis of samples starts.

Figure 4 shows the cupric ion concentration using the spectrophotometer. The case of Base (black line) is the distilled water. So, the cupric ion concentration is zero. The bulk case (red line) is the sulfuric acid–copper sulfate (H_2SO_4–$CuSO_4$) solution. This case presents the maximum value among others. The case of 300 mV (blue line) and 600 mV (Pink line) is an initial voltage and the voltage of limiting current range, respectively. The cupric ion concentration of the initial voltage is similar to the bulk solution. And then the value of limiting current range becomes smaller. The variation of the cupric ion concentration according to the voltage was confirmed by this method.

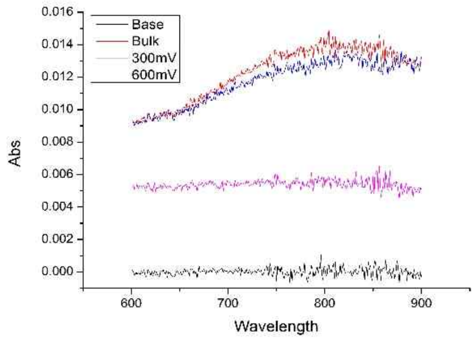


Fig. 4. The results for the spectrophotometer.

3.4 Interferometry

Interferometry makes use of the principle of superposition to combine waves. When two waves with the same frequency combine, the resulting pattern is determined by the phase difference between the two waves. Interferometry is widely used in science and industry for the measurement of small displacement, refractive index changes, etc. [10].

The arrangement of interferometry is schematically illustrated in Fig. 5. A laser beam emitter was used as the light source. The laser beam is divided into two light beams by a beam splitter. One beam, the reference beam, is reflected by a mirror and reaches the detector (H) directly. The other beam, the object beam, is collimated to the same diameter by beam expander. After passing through the test section (electrolytic cell), it is joined with the reference beam on the same detector (H). When both beams recombine at the detector, the interference patterns are formed.

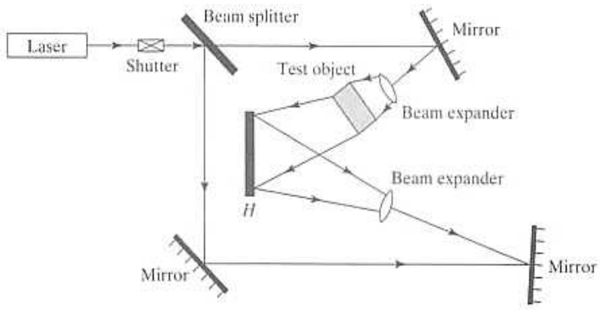
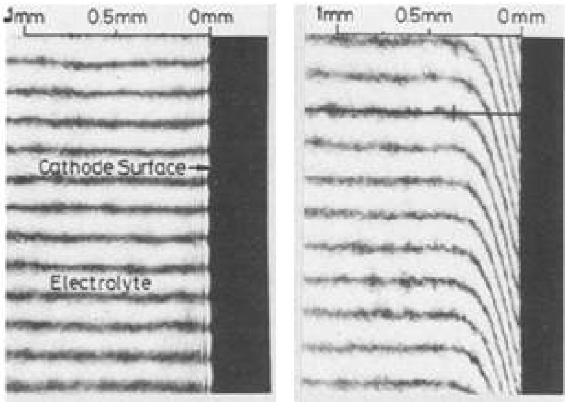


Fig. 5. The typical arrangement of interferometry [10].

Yasuhiro and Yoshio carried out an experimental study on the measurement of cupric ion concentration in the diffusion layer using the interferometry [11]. When the electrolysis in the electroplating system starts, the diffusion layer depending on the variation of cupric ion concentration is accompanied by natural convection along the electrode.

Yasuhiro and Yoshio reported the interference pattern in Fig. 6 [11]. Before the start of electrolysis, patterns were parallel as shown in Fig. 6(a). After the start of electrolysis, this pattern was shifted due to the concentration gradient formed in the diffusion layer. The relationship between the change of the refractive index of the solution and the pattern shift is calculated by the interference equation. If know the change of the refractive index of the solution using the interferometry, the variation of cupric ion concentration can be obtained.



(a) (b)

Fig. 6. The interference pattern before (a) and after (b) the start of electrolysis.

4. Conclusions

This work devised a method to simulate the different cooling conditions of the top and side walls. The electrical resistance was adopted to the top plate. But the quantitative temperature conditions depending on the electrical resistance were unknown. In order to overcome the limitations of mass transfer, this work tried to measure the cupric ion concentration.

The methods of concentration measurement are RGB, Brightness, ICP, PIV, and Interferometry. The key of RGB, Brightness and PIV method is the clear images of the concentration boundary layer corresponding the thermal boundary layer of heat transfer. The results for ICP method can be got by taking the trace sample of a solution, accurately. The formation of patterns in the interferometry is very important. The characteristics of the interference pattern depend on the nature of the light source, the precise orientation of the mirrors, etc. The methodology of concentration measurement is still under development stage.

In order to develop the methodology of concentration measurement, the improved photographic technique and accurate sampling are required. As the acryl is also inhomogeneous, the interference pattern is unstable. So the test section will be redesigned by using the optic window that minimized the refractive index.

ACKNOWLEDGEMENT

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