Numerical Analysis of the Thermodynamic Stability of Aqueous Cu-Ni-S-H₂O System for the Preparation of Thin Copper-Nickel Multi-nano-Layers by Using Pulse Electro-forming

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ABSTRACT

Thermodynamic solution stability of aqueous copper-nickel-sulfur system was numerically analyzed to produce thin copper-nickel nano-multi-layers by pulse electro-forming. The main program for numerical analysis was written by C# language, which was composed of the data input, numerical calculation, decision and plotting sub-programs. From the thermodynamic data of 32-feasible phases of the Cu-Ni-S-H₂O system, the phase stability diagram of the Cu-Ni-S-H₂O system was constructed. It revealed the electro-forming condition of the copper and the nickel was $V_{SHE}<0.35$ for copper deposition, $V_{SHE}<-0.24$ for nickel deposition, pH=1.0 and 25°C in the sulfide bath. The copper-nickel multi-layers was well produced by electro-forming in the sulfide bath with two-wave pulse voltages of $-0.2V_{SHE}$, -0.5 mA/cm², and 25 seconds for copper deposition and $-1.7\ V_{SHE}$, -50 mA/cm² and 80 seconds for nickel deposition, at pH=1.0 and 25°C. From TEM and EDX analysis the Cu-Ni multi-layers with about 5 μm thick had the copper-rich phase of about 20 nm in thick and the nickel rich phase of about 25 nm in thick, respectively.

Key Words : numerical analysis, computer simulation program, thermodynamic solution, pulse electro-forming

1. Introduction

The pulse electro-forming is one of economically useful wet methods to produce thin metal sheet by electro-deposition upon a mandrel that is subsequently separated from the deposit. Thus, researches to study materials has been attractive attention to produce a commercial alloy sheet by using electro-forming process [1]. There are several electro-formed metals underdeveloped or developed for nowadays electronic industries such as copper mesh for electron magnetic conductor (EMC), nickel stamper for information display parts, iron-nickel alloy for micro-electro-mechanical systems (MEMs) of electronic parts and metal matrix composites with ferrite nano-particles for electro-magnetic insulator (EMI) [2-4]. One of problems of the pulse electro-forming for the preparation of alloy sheet is difficulty of controlling an aqueous solution because the ion concentration of the aqueous solution is changed during electro-forming process due to the continuous deposition of metallic ions on the electrode and the change of the concentration polarization in front of electrode. One of the solution to overcome the pulse electro-forming problems is completely understand the thermodynamic stability of a solution for electro-forming and precisely control the aqueous solution chemistry, especially for the preparation of alloy deposition.

Thermodynamics of aqueous solution is well introduced by Pourbaix diagram, which is based on the Gibb's free energy of ionic spaces and phases in aqueous solution [5]. The Pourbaix diagram delineates the relative thermody-namic stabilities of various chemical species in aqueous solution which shows the range of stability of aqueous

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species as well as solid phases under specified conditions of the oxidation potential (Eh) and the hydrogen activity (pH).

However, many of important aqueous systems in field are complicated by the presence of complexing ligands of which aqueous stabilities change with solution conditions, total plotting space of the Eh-pH must be considered in terms of sub-diagrams. In case of the thermodynamic stability of m-number of species, $m(m-1)/2$ equations relating all possible pairs of species should be systematically considered. It becomes quite time consuming calculations as the number of species increases. Accordingly a numerical approach by using a computer is useful for a rapid calculation and plotting of species predominance fields in terms of activity composed of the dissociation equations of each phase, balancing variables, matrix notation, generation of relative stability equations, and determination of stability domains [6,7].

The dissociation equation of each phase is written in terms of certain set of compounds or variables. The reaction coefficient of each phase and variable should be specified. The balancing variables is for comparison of the relative stability of two phases to be determined by a single equation. Matrix notation is for the numerical solution which consists of m-phases and n-variables. The generation of relative stability equations is for linking all the possible pairs of phases. The determination of stability domains is for systematic scanning of the plotting area to determine phase boundaries by calculation.

Although the Metal-H-O diagrams at room temperature and unit atmosphere were well reported by the work of Pourbaix, little information about systems including additional elements either as species in an aqueous phase or alloys in a metal and at high temperature or high pressure conditions are available because of little thermodynamic information of complex phases in multi-element system at a special conditions [8]. Especially, little information about the applications of the aqueous phase diagram to make the nano- phase layers by the electroforming is available.

Hence, the objectives of this study are to develop a program for expecting the thermodynamic stability of aqueous solution, especially, copper-nickel-sulfur system to produce an optimum pulse-electro forming condition for the preparation of the thin copper-nickel multi-nano-layers for high performance electro-magnetic conductors.

2. Experimental Method

2.1 Construction of phase stability diagram of aqueous Cu-Ni-S system

Table 1 is the Gibbs free energies of various species of the aqueous copper-nickel-sulfur system for the construction of Eh-pH diagram to know the phase stability, in which the 32 numbers of phases were considered for the 496 number of phase equilibrium relating all possible pairs of species. The thermodynamic data of Table 1 were obtained from JANAF thermodynamic data book [9]. Fig. 1 is a flowchart for computing the construction of the aqueous Cu-Ni-S system.

The simulation program to determine the aqueous phase stability of Metal-H₂O system was written by C# language. The program was made up of sub-programs for the data input, numerical calculation, decision and plotting. The data input part sub-program consisted of the array for the number of phase, variables, components, reaction temperature and pressure which were considered. The input part sub-program was for systematical generation of the $m(m-1)/2$ numbers of stability equations relating all possible pairs of species.

The numerical calculation sub-program was for the determination of the Gibb's free energy change and the equilibrium constant for each reaction equation. The decision sub-program was for the determination of the stable phase for the reaction at a given oxidation potential (Eh) and hydrogen activity (pH) based on the equilibrium constant obtained by the numerical calculation sub-program. The plotting part was to divide the Eh-pH area as very small grid to represent the gride-to-grid stable phase determination and draw the lines.

Table 1. Aqueous reaction and standard Gibb's free energy for the calculation of phase stability of Cu-Ni-S- H₂O system [9]

Species	H₂O	e⁻	H⁺	Cu/Ni/S	G° [cal/mole]
Cu^{2+}	0	-2	0	1	15,530
Cu^+	0	-1	0	1	12,000
Cu_2O	1	-2	-2	2	-34,980
CuO	1	-2	-2	1	-30,400
$HCuO_2^-$	2	-2	-3	1	-61,420
CuO_2^{2-}	2	-2	-4	1	-43,500
$Cu(OH)_2$	2	-2	-2	1	-28,610
Cu	0	0	0	1	0
NiO	1	-2	-2	1	-51,610

| Species	H_2O	e^-	H^+	Cu/Ni/S	G° [cal/mole]
Ni_3O_4	4	-8	-8	3	-170,150
Ni_2O_3	3	-6	-6	2	-112,270
NiO_2	2	-4	-4	1	-51,420
Ni_2^+	0	-2	0	1	-11,530
$HNiO_2^-$	2	-2	-3	1	-83,465
$Ni(OH)_2$	2	-2	-2	1	-108,300
Ni	0	0	0	1	0
H_2S	0	2	2	1	-6,540
HSO_4^-	4	-6	-7	1	-179,940
$S_2O_8^{2-}$	8	-14	-16	2	-262,000
SO_4^{2-}	4	-6	-8	1	-177,340
$HS_2O_3^-$	3	-4	-5	2	-129,500
$S_2O_3^{2-}$	3	-4	-6	2	-127,200
HS^-	0	2	1	1	3,010
S^-	0	2	0	1	21,958
S	0	0	0	1	0
CuS	0	0	0	2	-7,667
Cu_2S	0	0	0	3	-1,856
$CuSO_4$	4	0	-8	2	-186,810
NiS	0	0	0	2	-20,369
NiS_2	0	0	0	3	-29,834
Ni_3S_2	0	0	0	5	-35,571
$NiSO_4$	4	0	-8	2	-158,095
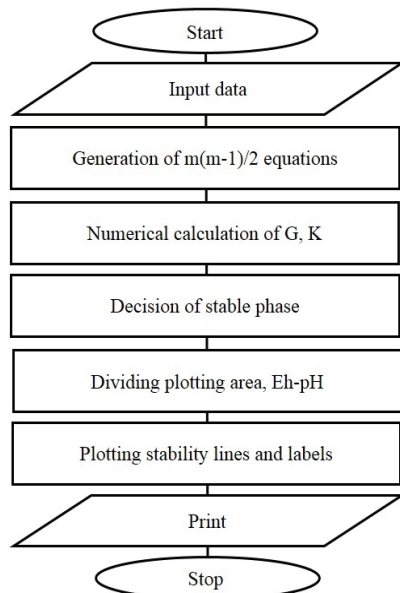
Fig. 1. Flowchart for computing the construction of the aqueous phase equilibrium diagram.

2.2 Specimen preparation

Pulse electro-forming for the preparation of the thin copper-nickel multi-nano-layers was carried out in a modified sulfate bath including $CuSO_4$ (Samchun, >99.0%, Korea), $NiSO_4$ (Samchun, >98.5%, Korea), $Na_3C_6H_5O_7$ (Sigma Aldrich, >99.0%, USA), H_2SO_4 and NH_4OH at 25ºC by two-wave pulse plating rectifier (Jisan, Korea) at room temperature. The anode and the cathode were titanium mesh and copper plate, respectively. The pulse voltage was selected based on the aqueous Cu-Ni-S phase stability diagram.

2.3 Chemical analysis and microstructure observation

Microstructure was observed by transmission electron microscopy (Jeol JTM 2010-F, Japan). The TEM sample was prepared by focused ion beam (FIB, JIB-4000, Japan) workstation. Chemical analysis was carried out by energy dispersive spectroscopy (EDS, Oxford, UK).

3. Results and Discussion

3.1 Verification of a phase stability program

In order to verify the phase stability program which made in this study, Cu-H_2O system was constructed and compared with the previous results [5]. Fig. 2. is the typical input file for a Cu-H_2O phase stability made in this study. As shown in Fig. 2., 4-species like Cu, Cu^{+2}, CuO, and Cu_2O generated 6-equations relating all possible pairs of the 4-species with the standard Gibb's free energy change for the determination of equilibrium constants of each reaction. Fig. 3. is the Eh-pH diagram of the aqueous Cu-H_2O phase diagram constructed by this study. It is well agreement with a previous result [5]. It means that the phase stability program prepared in this study is completely working.

3.2 Construction of phase stability diagram of aqueous Cu-Ni-S system

In this study, the phase stability of the Cu-Ni-S-H_2O system was considered to produce the copper and nickel deposits in a sulfide solution. The feasible solid phases of the Cu-Ni-S-H_2O system were selected as nickel sulphide (Ni_3S_2), copper sulphide (Cu_2S), various oxides like NiO and CuO based on the literature survey [9, 10]. Since the copper ions (Cu^{+2}) reacted with the solid phases. At a high

pH, possible reactions like $Cu_2O + 4H^+ + 0.5\ O_2 = 2Cu^{2+} + 2H_2O$, $Ni_3S_2 + 2H^+ + 0.5O_2 = Ni^{2+} + 2NiS + H_2O$ and $Ni_3S_2 + 2Cu^{2+} = Cu_2S + NiS + 2Ni^{2+}$, $Ni_3S_2 + 2Cu^{2+} + 0.5O_2 = 2NiS + Ni^{2+} + Cu_2O$, $Cu^{2+} + H_2S = CuS + 2H^+$ were considered.
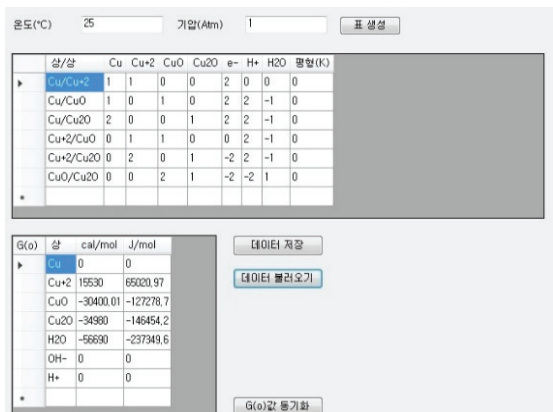

Fig. 2. Typical input for the verification of the numerical construction of Eh-pH diagram of Cu-H$_2$O at room temperature.
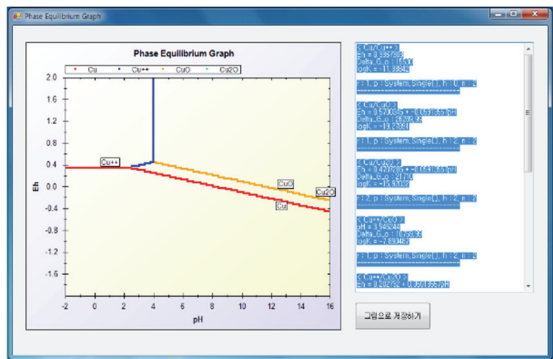

Fig. 3. Eh-pH diagram of Cu-H$_2$O system at 25ºC.

Fig. 4. is the thermodynamic phase stability of aqueous Cu-Ni-S-H$_2$O system at 25ºC obtained by the numerical calculation with a computer program made by this study. As shown in Fig. 4., it is clear that the copper and the nickel can be electro-deposited at the critical conditions of $V_{SHE} < 0.35$ for copper deposition and $V_{SHE} < -0.24$ for nickel deposition, pH < 1.0 and 25ºC by using pulse plating. Considering the obtained conditions, the pulse electro-forming to make the copper-nickel multi-layers was carried out in the modified sulfate bath.
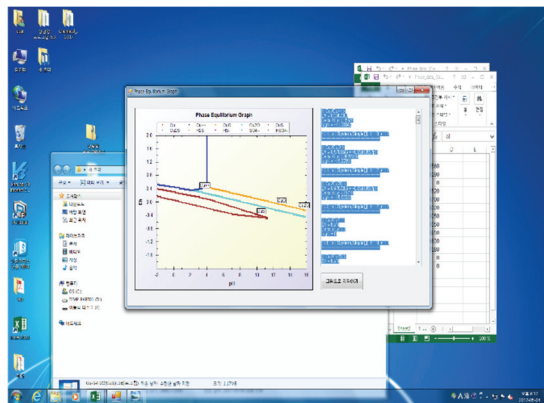

Fig. 4. thermodynamic phase stability of aqueous Cu-Ni-S-H$_2$O system at 25ºC.

3.3 Microstructure observation and chemical analysis

Since the numerical approach showed the possibility and the condition to produce the copper-nickel layers by electroplating, the pulse electro-forming was carried out in a modified sulfide bath at room temperature by pulse current to make the copper-nickel multi-nano-layers. The voltage, current density and plating time were selected such as $-0.2V_{SHE}$, -0.5 mA/cm^2, and 25 seconds for copper deposition and -1.7 V$_{SHE}$, -50 mA/cm^2 and 80 seconds for nickel deposition. The current density was determined by the rectifier capacity due to the potential value. The plating time was selected based on the copper and nickel deposition efficiency.
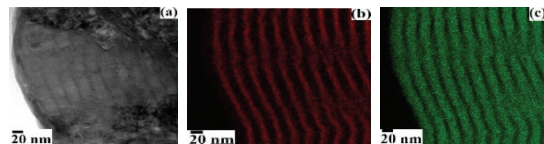

Fig. 5. Typical TEM images and EDX mapping of copper-nickel multi-nano-layers formed by pulse electro-forming (a) TEM image (b) Cu (c) Ni.

Fig. 5. is a typical TEM image and its chemical mapping of copper-nickel layers formed at the conditions given by the phase stability diagram determined by numerical analysis. As shown in Fig. 3-4, the copper-nickel multi-layers with nano-thickness were well formed by the pulse electroplating at the conditions of $-0.2V_{SHE}$, -0.5 mA/cm^2, and 25 seconds for copper deposition and -1.7 V$_{SHE}$, -50

mA/cm^2 and 80 seconds for nickel deposition, at pH=1.0 and 25°C. The electroformed multi-nano-layers was composed of the copper-rich phase of about 20 nm in thick and the nickel rich phase of about 25 nm in thick, respectively.

4. Conclusions

The computer program to determine the aqueous phase stability of multi-phases system was written by C# language. The main program was made up of the data input, numerical calculation, decision and plotting parts. The phase stability program was verified the output plot comparing with the previous results like Cu-H_2O system.

From the thermodynamic data of the 32 numbers of phases of Cu-Ni-S-H_2O system, the 496 numbers of phase equilibrium relating all possible pairs of species were considered and constructed the phase stability diagram of aqueous Cu-Ni-S-H_2O system. It supports that the copper and the nickel can be electro-deposited at the condition of V_{SHE}<0.35 (Cu), and V_{SHE}<-0.24 (Ni), pH< 1.0 by two-wave pulse plating.

Copper-nickel multi-nano-layers were well formed by pulse electro-forming in a modified sulfide bath with the conditions of –0.2V_{SHE}, –0.5 mA/cm^2, and 25 seconds for copper deposition and –1.7 V_{SHE}, –50 mA/cm^2 and 80 seconds for nickel deposition, at pH=1.0 and 25°C, which produced the copper-rich phase of about 20 nm in thick and the nickel rich phase of about 25 nm in thick, respectively.

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