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THERMAL DIFFUSION OF ^{57}Co INTO Rh FOIL FOR PREPARING MÖSSBAUER SOURCE

To establish the coating conditions for ^{57}Co, non-radioactive Co ions are dissolved in an acid solution and electroplated on to a rhodium plate. The thermal diffusion of electroplated Co into a rhodium matrix was studied to apply a ^{57}Co Mössbauer source. The procedure to form a Co deposited onto Rh foil was established using two different electroplating baths: the acid-based buffer (pH 3) containing boric acid, sodium chloride, and saccharin, and the alkaline-based buffer (pH 10) containing hydrazine hydrate and ammonium citrate. The influence of different annealing conditions was investigated. From the results, the best diffusion degree of electrodeposited Co onto the rhodium matrix was obtained in an annealing process performed at 1100°C for 3 h in vacuum over10^{-5} hPa.

Keywords: Mössbauer Source, Diffusion, Electroplating, ^{57}Co/Rh

1. Introduction

The most frequently used source for the Mössbauer spectroscopy is the ^{57}Co/Rh source, which was diffused ^{57}Co onto a rhodium (Rh) substrate [1]. The Mössbauer spectroscopy requires sources that emit narrow un-split lines. The ^{57}Co/Rh source is fabricated as follows: the first step electroplating a ^{57}Co required radioactive isotope onto the surface of an Rh substrate, and the second step is for thermal diffusion at high temperature into its crystal lattice [2-3]. Well-known methods developed for the electrodeposition of cobalt are inadequate for the electroplating of carrier-free isotopes. Such techniques require the deposition of sub-microgram quantities of the isotope from a bulk electrolyte containing no other impurities such as deliberately introduced metal ions [3]. For the deposition of pure cobalt, optimization of the electrolysis parameter is required.

In a previous study, it is well known that ^{58}Ni electroplating onto the target materials is the first process to produce ^{57}Co. An enriched isotope ^{58}Ni is prepared using vaporizing nickel powders with a laser and centrifuging the metal nickel gas. This ^{58}Ni is dissolved in an acid solution for making an electroplating buffer. After the process of ^{58}Ni electroplating onto the target materials, ^{58}Ni was irradiated with a proton beam [4]. An electroplating process was applied to form radioisotope ^{57}Co onto a metal sheet [5-6]. To remove the gamma ray recoil energy of ^{57}Co, it was diffused into metals such as Cu, Au, Fe, Pt, Rh, and Pd. The metals which have a high melting point and large mass (atomic weight) to make the recoil energy of ^{57}Co zero are suitable for a substrate such as Rh and Pd [7-8]. ^{57}Co diffused uniformly onto a metal Rh substrate is in a state capable of gamma ray resonance with adjacent materials. Rh matrix is

an applicative material for a high solubility of Co atoms and provides a good recoilless fraction [9-10].

In this study, a Co-plating solution is prepared using two different baths. One is an acid-based buffer (pH 3) containing boric acid, sodium chloride, and saccharin. The rest is the base-based buffer (pH 10) containing hydrazine hydrate and ammonium citrate. The optimization of the electroplating parameters for the deposition of Co on rhodium was considered as indispensable. The influences of current density, and pH of the electrolyte were investigated and described in this paper. In addition, the aim of this work was a determination of the optimal parameters for thermal diffusion of the electroplated Co into the Rh structure.

2. Experimental

A series of experiments were performed in order to determine the optional conditions for electrodeposition of Co on Rh foils with a thickness of 4.5 μm. The composition of alkaline electrolyte was ammonium citrate (25g/l), hydrazine hydrate (25g/l), and ammonia solution (25%) for adjusting the pH to 10. The acidic electrolyte contained in 0.1 M HCl and 0.1M NaCl in such proportions so as to assure a pH of 3. The volumes of the electrolytes were 10 ml. Charged cobalt (Co) ions are formed by chloride. The concentrations of Co in both the alkaline electrolyte and the acidic bath used in these experiments were 10^{-2} mg/ml. A platinum foil was used as the anode. The deposited Co was diffused almost completely into a rhodium matrix without a substantial loss at an annealing temperature from 1100 to 1200°C for various times under a vacuum or inert gas of Ar. The deposition yield was measured by the concentration of Co in the bath before

and after deposition using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The Co diffused Rh layer was identified using a Scanning electron microscope (SEM).

3. Results and discussion

[57]Co plating is similar to other electroplating processes that employ insoluble metal anodes. Specifically, it requires the passage of direct current (DC) between two electrodes that are immersed in a conductive, aqueous solution of cobalt salts. The flow of a DC causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with cobalt. The cobalt in the solution is present in the form of divalent positively charged ions (Co^{2+}). When the current flows, the positive ions react with two electrons ($2e^-$) and are converted into metallic cobalt (Co^0) at the cathode surface [11]. The reverse occurs at the anode where metallic cobalt is dissolved to form divalent positively charged ions that enter the solution. Co deposition was produced at a current density of 20 mA/cm^2, a bath temperature of 27°C, and various pH levels at 3 and 10. It was reported that the thickness of the electroplates can be controlled by the current density and deposition time [12]. Here, the relationship between the current density and plating time was determined in order to realize equal electric quantities for each condition. The rate of deposition for [57]Co on Rh foil with a thickness of 4.5 μm as a function of pH is shown Fig. 1. Definitely, lower values have been obtained for a chloride electrolyte (pH 3) than for a citrate electrolyte (pH 10). The rate of deposition shows almost a linear function of deposition time at and below 4h. Thus, the deposition time below 4 h was adjusted to achieve an average thickness based on Faraday's low for the electroplating of Co [13]. If the deposition time is increased, the rate of deposition is saturated [3].
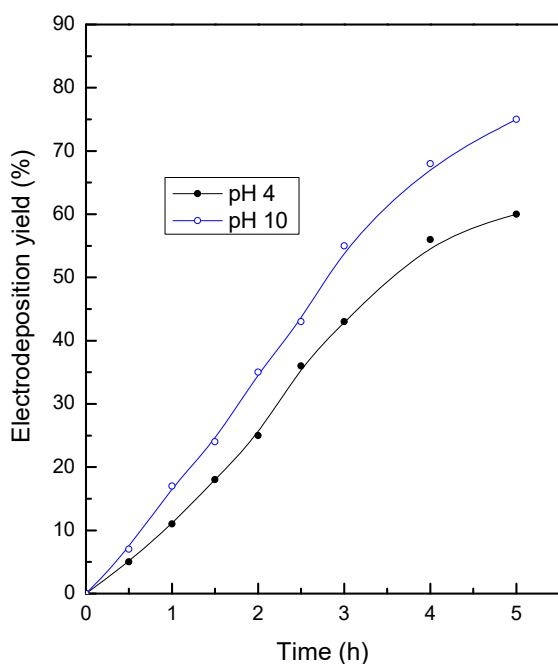
Figure 2 shows the results of XRD for the deposited Co on a Rh foil under the plating condition of pH at 10 and 3. XRD patterns were observed showing that the crystal structure of the Co deposits is pure hcp (hexagonal close packing). Six characteristic peaks at around 2θ are 42.3°, 48.2°, 72.2°, 76.0°, 87.0° and 92.0°,which is consistent with the (100), (002), (101), (102), (110) and (112) lattice plane diffractions of Co crystals, respectively, which are definitely observed for the Co particles.
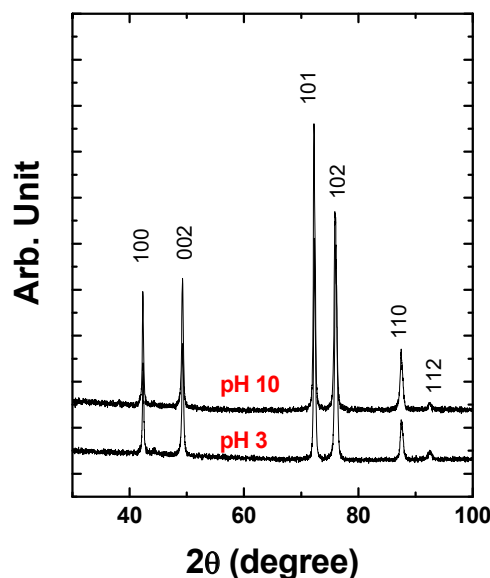

Fig. 2. XRD patterns of the Co deposits on Rh-foil

For the initial annealing attempts, Co electroplated Rh foil with thickness of 4.5 μm was used, and a relatively low vacuum of 10^{-2} hPa under an inert Ar gas atmosphere was maintained during the diffusion process. In addition, the annealing process was performed at a higher vacuum of 10^{-5} hPa in quartz and ceramic tubes at different temperatures. The detail annealing conditions are presented in Table 1.

TABLE 1

Thickness of coating layer of Co and annealing condition for Co/Rh

Sample	Plating Thickness	Heating Condition	
1-1	4.5 μm	1100°C – 1h	10^{-2}hPa / Ar
1-2	4.5 μm	1100°C – 3h	10^{-2}hPa / Ar
1-3	4.5 μm	1100°C – 5h	10^{-2}hPa / Ar
2-1	4.5 μm	1200°C – 1h	10^{-2}hPa / Ar
2-2	4.5 μm	1200°C – 3h	10^{-2}hPa / Ar
2-3	4.5 μm	1200°C – 4h	10^{-2}hPa / Ar
2-4	4.5 μm	1200°C – 5h	10^{-2}hPa / Ar
3-1	4.5 μm	1100°C – 1h	10^{-5}hPa / vacuum
3-1	4.5 μm	1100°C – 2h	10^{-5}hPa / vacuum
3-3	4.5 μm	1100°C – 3h	10^{-5}hPa / vacuum

Fig. 3 shows SEM images for the surface morphology and cross-section for Co electrodeposited Rh foil. The Co particles on the Rh plate had a spherical shape. The particles are diffused into an Rh matrix after annealing. Both Co and Rh particles are observed on the surface layer after annealing, as shown in

Fig. 1. Deposition rate for different pH electrolytes

Fig. 3d. The mapping images of elemental energy dispersive spectrum (EDS) for the cross section of Co coated Rh foil. The Co particles are observed on the surface of the Rh plate, only.

Figs. 4, and 5 show the mapping images of EDS for the cross section of Co coated and diffused Rh foil. The results also indicate that the synthesized final products were composed by Co particles on the surface of Rh foil. In a previous study, a relatively low vacuum 10^{-2} hPa under an inert Ar gas atmosphere was maintained during the diffusion process [4-5]. The diffusion yield of Co atoms into the Rh matrix is increased, with the rise in both the annealing temperature and heating time. The optimum conditions for the homogeneous diffusion of Co are determined as the annealing temperatures at 1200°C for 3h as well as at 1100°C for 5h, as shown in Fig. 4. The brightness of the greenish spots for Co particles is faint in the whole mapping region of the EDS. An inhomogeneous mapping spectrum is observed at an annealing temperature of 1200°C for 5h due to rapid aggregation of Co particles compared to the diffusion rate.
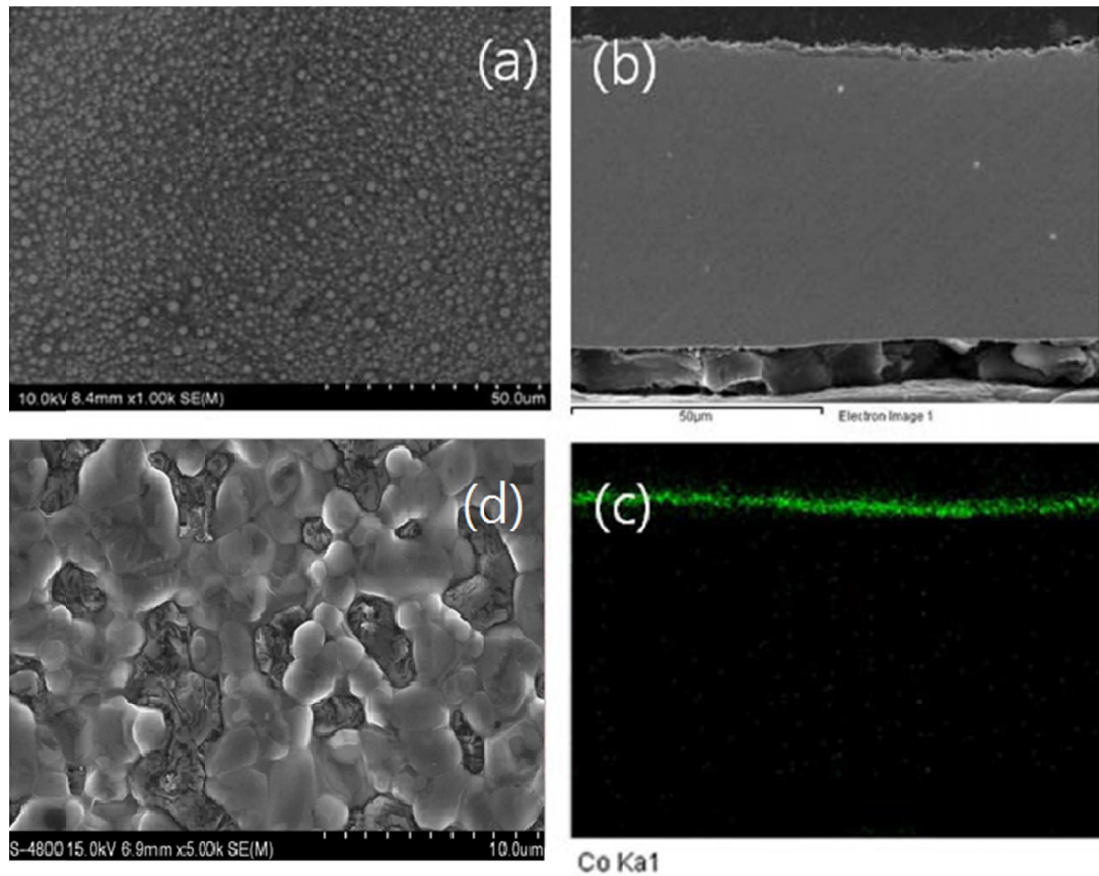

Fig. 3. SEM images for (a) surface of Co layer on Rh foil, (b) cross section images for Co coated Rh foil. Mapping of EDS for (c) Co layer in SEM image of (b), and (d) surface of Co-layer after annealing at 1100°C for 3 h
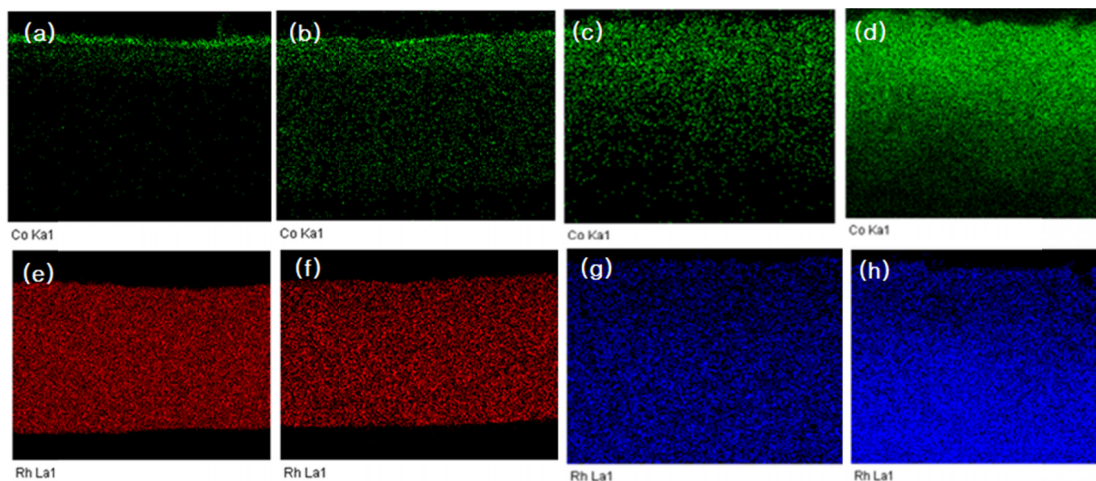

Fig. 4. Mapping of EDS for Co layer annealed under low vacuum using Ar inert gas at 1100°C for (a) 1 h, (b) 5 h, and at 1200°C for (a) 3 h, and (b) 5h. (e),(f),(g), and (h) are those of Rh layer
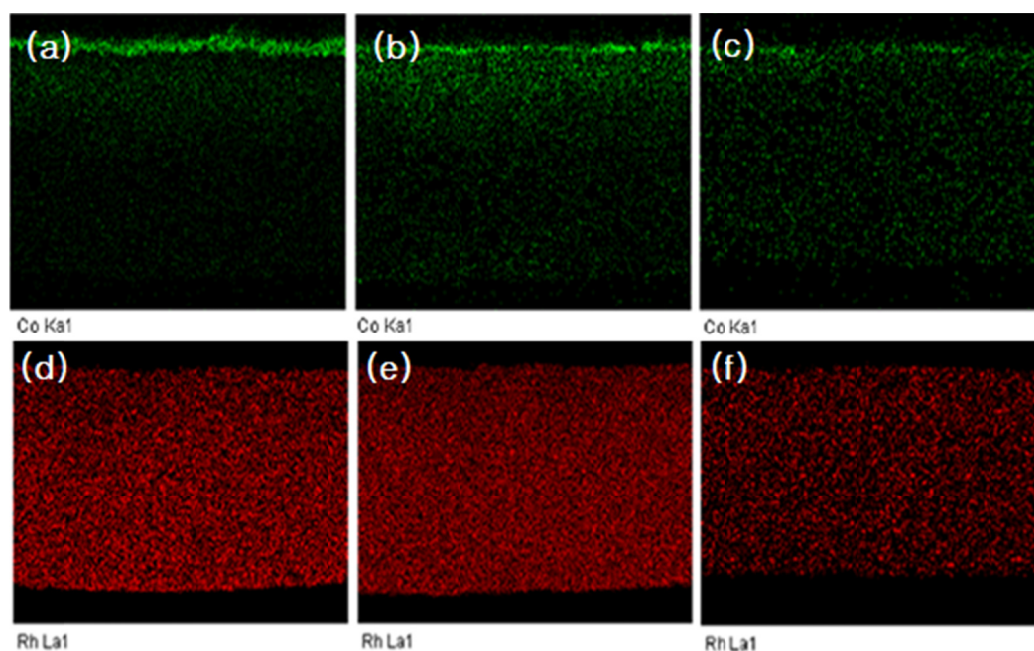
Fig. 5. Mapping of EDS for Co layer annealed at 1100°C for (a) 1 h, (b) 2 h, and (c) 3 h, and Rh layer for (d) 1 h, (e) 3 h, and (f) 5 h under high vacuum over 10^{-5} hPa

In this study, the annealing process was also performed at a higher vacuum of 10^{-5} hPa in quartz and ceramic tubes at different temperatures. The annealing temperature is fixed at 1100°C. The annealing time is increased from 1 to 3 h. The optimum conditions for the homogeneous diffusion is determined at annealing temperatures of 1100°C for 3 h, under a high vacuum atmosphere, as shown in Fig. 5. The brightness of both greenish and reddish spots for Co and Rh particles, respectively, is faint in the EDS. As the annealing condition is changed to a high vacuum (over 10^{-5} hPa), both the annealing temperature, and heating time are decreased compared to those carried at a low vacuum (10^{-2} hPa).

We were able to establish a prototype for the electroplating radioactive ^{57}Co and diffusion conditions. For Mössbauer investigations, the electroplated and annealed foil is mounted into a Ti capsule sealed with epoxy or brazed Be window [15]. All Mössbauer measurements were carried out on a pure iron foil (25 μm thick) as an absorber. The proposed condition in this study could be applied to prepare a radioactive career free ^{57}Co/Rh Mössbauer source Radioactive ^{57}Co (0.26 mCi) was deposited on Rh foil.

4. Conclusions

To establish the preparation of a Mössbauer source of ^{57}Co/Rh, natural Co was electroplated on the Rh plate. Both the acid-based buffer (pH 3) and the alkaline-based buffer (pH 10) are used for the plating bath. The deposition yield of the alkaline electrolyte is relatively higher than those of the acidic bath. The optimum conditions for the homogeneous diffusion are determined at annealing temperatures of 1100°C for 3h under a high vacuum atmosphere (10^{-5} hPa). The proposed condition in this study was applied to prepare a ^{57}Co/Rh Mössbauer source.

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