The Relationship between Microstructure and the Thermal Equilibrium Diagram of Au-Co Alloy Electrodeposit\(^*1\)

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An Au-Co alloy with an extensive composition range was electrodeposited from a gold sulfite and cobalt sulfate mixture. The Au-Co alloy electrodeposits were analyzed by XRD and TEM and the relationship between the phase and thermal equilibrium diagrams was investigated. The Au-Co alloy electrodeposits formed a solid solution over an extensive composition range. It was also revealed that the composition of the electrodeposited Au-Co alloy was equal to that of the quenched phase at a high temperature, about 950 °C.

\(\text{Keywords: gold sulfite, cobalt sulfite, gold-cobalt alloy, electrodeposits, microstructure, phase, equilibrium diagram}\)

1. Introduction

The physical and chemical properties of plated films depend on the crystallographic structure. Therefore, an understanding of the microstructure of plated films is required in order to control the physical properties of the films. Many studies of plated films have been reported, such as chemical or electrochemical reactions on the surface of electrodes;\(^1\)–\(^5\) however, there have been few studies of crystallographic structure.

The relationship between various plated films and thermal equilibrium diagrams was investigated. As a result, the microstructures of plated films were found to be composed of amorphous, meta-stable, or supersaturated solid solution, and these phases were not dependent on plating conditions, such as over-potential, anionic species, pH etc., but were dependent on the composition of the plated film.\(^6,7\) From the appearance of a meta-stable phase, it was considered that the plated films were composed of a structure as a result of quenching from high temperature.

In this study, Au-Co alloy plated film was investigated. The thermal equilibrium diagram of Au-Co alloy shows a eutectic type, as shown in Fig. 1(A). The Au-Co alloy is not composed of Au or Co solid solutions of each other at normal temperature, but Co atoms can fuse into gold crystals up to 23.7 at% and a few at% of Au can fuse into Co crystals at the eutectic temperature (996 °C). Au-Co alloy is often referred to as hard gold and it is generally used for contact components requiring good resistance to corrosion, abrasion, and a high hardness.\(^3\) Consequently, several studies of Au-Co alloy plated films have been reported;\(^3\)–\(^11\) however, those studies were limited to Au-Co alloy compositions with only a few at% Co that are used for practical application. Therefore, the relationship between microstructure and the thermal equilibrium diagram of Au-Co plated films over the entire composition range was investigated in this study.

Fig. 1 Thermal equilibrium diagram of Au-Co alloy (A), and phase diagram of the deposited Au-Co alloy film obtained in this investigation (B).

2. Experimental

The composition and conditions of the electroplating bath are given in Table 1. The plating bath solution was composed of a mixture of sodium gold sulfite and cobalt sulfate solutions. The useful pH range of each bath differs, with pH 6.2 to 8.5 in a sodium gold sulfite bath and pH 1.0 to 5.0 in a cobalt sulfate bath, so that a mixture of these solutions cannot be prepared without precipitation and decomposition of sodium gold sulfite. Therefore, the pH was shifted to a neutral range using sodium gluconic acid prior to addition of sodium gold sulfite. The total molecular concentration of Au + Co is maintained at 0.2 mol/L and the bath compositions were varied with molecular ratios of Au : Co at 1 : 4, 1 : 9 and 1 : 14. The plating bath temperature was maintained at 50°C. The current density was varied from 10 to 1000 A m\(^{-2}\) and the plating time maintained at 40 C. A direct current (DC) source was employed for constant current plating with a Pt/ Ti mesh anode (Pt plated on Ti mesh), and a magnetic stirrer was used for agitation of the plating solution. Ni-P films were deposited by electroless plating (363 K, 600 s, 2 μm thick) on
electropolished Cu plates and these were used as substrates to investigate the structure of the Au-Co alloy films without the influence of crystallographic orientation. The substrates were entirely covered with insulating tape except for the deposition area (10 × 20 mm). However, the nickel from the substrate is substituted with Au, because of nickel immersion as soon as the substrate is dipped in the plating bath. Therefore, 100 μm strike gold plating was performed to prevent this substitution. It was confirmed that the gold strike plating film was composed of fine crystals and was almost amorphous with no peaks or crystallographic orientation observed by X-ray diffraction (XRD).

The surface morphologies of films were observed by scanning electron microscopy (SEM; Hitachi S-4500) and a quantitative analysis of the compositions of Au and Co was made using an energy-dispersive X-ray spectrometer (EDX; Horiba EMAX5770) attached to the SEM. Cathode polarization was examined using a potentiostat, and a Ag/AgCl electrode was used as the reference electrode. The phase structure of the films was analyzed by XRD and transmission electron microscopy (TEM; JEOL JEM-2010). The thin film samples used for TEM analysis were prepared with an ultramicrotome (ULTRACUT-N; Raichart Nissei Co., Ltd.). Heat treatment of the films was performed in a vacuum furnace for 1 hour at 300 ºC.

3. Results and Discussion

3.1 Current density and cobalt content in the films

Figure 2 shows the cobalt content in the films plated using various current densities and various bath compositions. The cobalt content increased with increasing current density for all bath compositions. The rate is remarkable at lower current densities from 5 to 20 A m⁻², but at higher current densities the cobalt content does not vary and is constant.

Figure 3(A) shows the current density and potential and the composition of Au-Co alloy deposits (B). The surface morphologies of films were observed by scanning electron microscopy (SEM; Hitachi S-4500) and a quantitative analysis of the compositions of Au and Co was made using an energy-dispersive X-ray spectrometer (EDX; Horiba EMAX5770) attached to the SEM. Cathode polarization was examined using a potentiostat, and a Ag/AgCl electrode was used as the reference electrode. The phase structure of the films was analyzed by XRD and transmission electron microscopy (TEM; JEOL JEM-2010). The thin film samples used for TEM analysis were prepared with an ultramicrotome (ULTRACUT-N; Raichart Nissei Co., Ltd.). Heat treatment of the films was performed in a vacuum furnace for 1 hour at 300 ºC.

3.2 XRD measurement of Au-Co alloy films

Figure 4 shows XRD patterns of Au-Co alloy films of each composition. The diffraction peaks for Au (111), (200), (220) and (311) appeared only for compositions of Au-5.1 at% Co to 51.3 at% Co, and the peaks then shifted to higher diffraction angles and broadened. Figure 5 shows the amount of peak shift for films with different Co content. Figure 6 illustrates the lattice constants for various Co content of deposited Au-Co films, calculated from the diffraction angle of the (111) peak. The solid line drawn connecting the lattice constant of Au (0.4078 nm) to Co (1:9) (A) and the composition of Au-Co alloy deposits (B).
measurements (Fig. 4) did not show diffraction peaks of the Co crystal, and the reason for this is undetermined. In our previous studies, the phase structure of Ag-Co alloy, Au-Ni alloy, and Au-Fe alloy plated films, the XRD peaks of the element with a higher melting point displayed broadening, indicating a fine crystalline form near an amorphous state. Therefore, it is considered that the Co crystal of Au-Co alloy films in this study is also composed of fine crystals that are almost amorphous. The higher Co content film at 78.5 at% Co does not display the diffraction peaks of a Au solid solution with Co fused into Au as stated above, but only broadened peaks appear at the range of 2θ = 40 to 50°.

### 3.3 TEM analysis of Au-Co alloy plated films

Figure 7 shows a TEM cross-sectional image of the higher Co content Au-78.5 at% Co plated film confirming that the film is composed of fine crystals and close to an amorphous state. The Au-Co alloy plated film can be observed on the Cu plate substrate plated with amorphous Ni-P. The Au strike plating film cannot be seen in the TEM image because it is extremely thin. The dark field image of the Au-Co alloy plated film shows fine crystals and diffraction rings of a high degree index appear in the electron diffraction pattern. It is therefore considered that this plated film is composed of an aggregate of extremely fine crystals. The peak of ε-Co (hcp structure) appears at 94.0 at% Co. However, the lattice constant of the c axis of the ε-Co crystal (0.4089 nm) is larger than the value reported in the JCPDS (0.4061 nm), and this is between the lattice constant of Au (0.4078 nm). This indicates that the ε-Co crystal fuses into the Au atoms. A film of this composition does not only display the peaks of a Au solid solution, but also the α-Co peaks. Therefore, it is considered that a plated film near a composition of 94.0 at% Co is composed of an aggregate of extremely fine crystals of Co crystals saturated with Au atoms.

The phase diagram of the Au-Co alloy plated film examined in this study is compared with the thermal equilibrium phase diagram, as shown in Fig. 1(B). From the results, it is considered that the structure of the Au-Co alloy plated film is composed of a metastable phase of Co supersaturated Au solid solution for a Co content less than Au-18.0 at% Co, and an aggregate of Au solid solution and supersaturated ε-Co at higher Co content. The eutectic structure of Au solid solution and ε-Co in the compositions from 18 at% Co to 94.0 at% Co is composed of extremely fine crystals, especially the Au-78.5 at% Co film with weaker diffraction peaks, is considered to be composed of very fine crystals for all the compositions.
It was determined that the Au-Co alloy plated films are not composed of thermally stabilized structures, but of metastable structures, such as the eutectic of a Au and Co supersaturated solid solution.

Figure 8 shows XRD patterns of the plated films after 1 hour annealing at 300°C. As a result of annealing, the Au (111) diffraction peaks are shifted to higher angle, and are in agreement with the angle given in JCPDS ($\theta = 38.2°$). The profiles of the peaks become sharp and indicate the growth of crystals as the plated film reverts from an amorphous-like state. Therefore, it is considered that the Co atoms that are fused and supersaturate the Au crystals, diffuse out of the Au crystals and the Au crystals become stable and grow larger. However, the Co crystals in higher Co content films do not grow and it is considered that these plated films are composed of stable crystals.

### 4. Conclusion

The structure of Au-Co alloy plated film is composed of Co supersaturated Au solid solution for Co content less than approximately 18.0 at% Co, and Au supersaturated ε-Co solid solution for Co content above approximately 94.0 at% Co. A eutectic structure of supersaturated Co and Au solid solution is found in the composition between 18.0 at% Co and 94.0 at% Co. The crystals of Au-Co alloy plated films are composed of an aggregate of very fine crystals at approximately 78.5 at% Co. Au-Co alloy plated films are composed of a quenched phase structure at 950°C, according to the thermal equilibrium state diagram.

### REFERENCES