Research to Prevent Discoloration of Silver Traditional Handicrafts

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Abstract: Why does silver (Ag), which are classified as precious metals such as gold (Au), platinum (Pt), and palladium (Pd), easily discolor in the atmosphere? The reason is that gold, platinum, and palladium do not react well with the discoloration atmosphere to the extent that they exist as metals in nature. However, although silver exists as natural silver, the amount is not large. Most of them exist in nature as silver oxide, silver chloride and silver sulfide. For people to use it, it is much more effective to reduce it to pure metallic silver than silver oxide, silver chloride, and silver sulfide (gloss, electrical and thermal conductivity, workability, etc.), so it is unstable by using reducing agents such as carbon monoxide or hydrogen gas. It is made of metal and used.In this study, as a result of conducting research to prevent discoloration of silver, the following results were obtained.1) If the power of about 1.5v 2nd battery was connected in the air, the discoloration of silver could be prevented by supply of electrons.2) It was possible to prevent discoloration of silver by promoting the electrochemical reaction by contacting aluminum anode, which is a more active metal than silver.

1 INTRODUCTION

The silver (Ag) metal classified as a noble metal such as gold (Au), platinum (Pt), and palladium (Pd), but it well discolored in the atmosphere. This is because gold, platinum, and palladium are not well reacted with the discoloration atmosphere to the extent that they exist in nature as a metal. But silver is a compound rather than a silver pure metal. Mostly silver oxide, silver chloride and silver sulfide exist in nature. In order to smelt pure metallic silver, it must be reduced by supplying energy from the outside. In this case, the produced metal is easily discolored due to internal energy non-uniformity and impurities (copper, tin, etc.). The silver metal is also supplied with energy from the outside when the external energy required for the reduction of silver is added and when it is made into chains or plates. Moving in the direction of reducing this energy is more stable, so it tends to discolor and decrease in intensity. For these reason, the metal is in an unstable state, so the metal itself is trying to return to stable oxides, sulfides and chlorides, which is why the color of the metal changes.

In particular, the discoloration is severe as shown in the following Fig. 1.

Figure 1: The causes of discoloration of silver are as follows. Silver metal is stable to water and oxygen but reacts with ozone (O3) to form silver oxide (Ag2O) and easily reacts with sulfur (S) or sulfur compounds (such as hydrogen sulfide, H2S) In this case, the color is discolored. This is because silver is blackened if it is used for a long time.

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4 Ag + O2 + 2 H2S → 2 Ag2S + 2 H2O
High temperature: Ag+(1/2)O2 =>AgO
Low temperature: Sulfide reaction (Ag+(1/2)S2 =>Ag2S)
Discoloration (Yellow->Brown -> Black)

Included in domestic household bathing agent (containing sulfur such as sodium sulfate and lactate), onion, gasoline burning (sulfur dioxide gas generation), shampoo, kitchen detergent (including surfactant), rubber product (rubber band etc.), household bleach The silver metal is discolored by the sulfur component.

At present, such discoloration problem cannot be solved and organic coating is applied to prevent contact with gas such as sulfur gas or chlorine gas. And alloy technology is used by adjusting the discoloration and strength by alloying the second element or the third element as shown in the following table. And silver plating and precious metals such as palladium and rhodium are electroplated on the silver surface to prevent discoloration, but the complete method has not been found yet.

For this reason, research is needed to prevent discoloration of silver metal products.

In this study, an experiment to prevent discoloration of silver products is conducted with an electrochemical idea.

2 EXPERIMENTAL METHOD

Ag alloy used in this study is to prevent oxidation by applying NaOH to Ag, Cu, and Nd in a graphite crucible with a size of 40x 40 x 25mm as shown in Table 1. It is melted at 1000°C and naturally stirred for 30 minutes. An alloy was produced by air cooling. The x-ray diffractometer (XRD, Rigaku Ultima IV).The structure was observed using a field emission scanning electron microscope (SEM, Hitachi S 4800), and the elements were mapped using an energy dispersive X-ray spectroscope (EDS), and the corrosion potential and current of each specimen were measured through a potentiometer (Versastat 4.0).In order to measure, a coincidence polarization test was performed. It was measured after grinding the specimen with #600 SiC Paper before measurement. The measurement range was from -0.4VSCE to 1.2VSCE, and a three-electrode cell was used. A saturation sensation electrode (SCE) was used as the reference electrode and a Pt network was used as the counter electrode, and the experiment was conducted using a 3.5 wt.% NaCl electrolyte.

The rate of discoloration between the 1.5V battery contacted with the silver metal product to form an electrochemical circuit and the battery not contacted was measured visually. In addition, the same experiment was performed for the presence or absence of contact of the sacrificial aluminum anode.

Table 1: Composition of silver alloy.

	92.5 wt % Ag -75 wt. % Cu	92.5 wt % Ag -75 wt.% Cu -0.5 wt. % Nd
Ag (g)	37	37
Cu (g)	3	2.8
Nd (g)	0	0.2
Total (g)	40	40

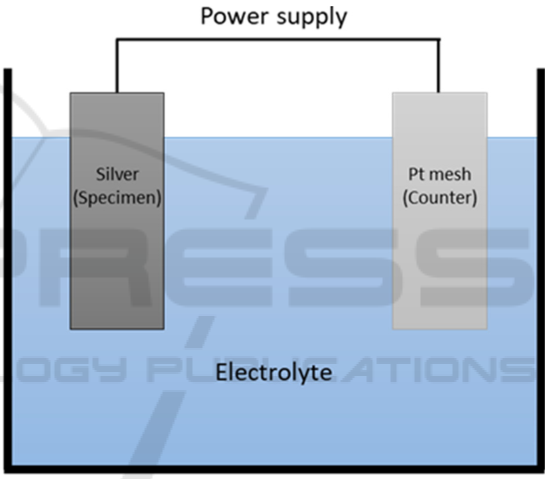

Figure 2: Schematic diagram of the experiment of ICCP device.

Fig. 2 shows the schematic diagram of the I.C.C.P(Impressed Current Cathodic Protection) experimental apparatus. It is a device that measures the discoloration of silver metal depending on whether electrons are supplied from the outside into the electrolyte, which is a corrosive atmosphere.

3 RESULTS AND DISCUSSION

The structure of the specimen to which 0.5wt% of Nd was added was observed through SEM, and the results are shown in Fig. 3. No secondary phase produced by the addition of Nd was found. In the sterling silver composition, which is an alloy of Ag and Cu, copper does not form a secondary phase of the alloy and is known to be dispersed in one size, and no other secondary phase was found even after the addition of Nd. According to the previously studied literature, it was confirmed that other phases do not exist in the composition used in the present study through the Ag-Cu-Nd ternary phase diagram.

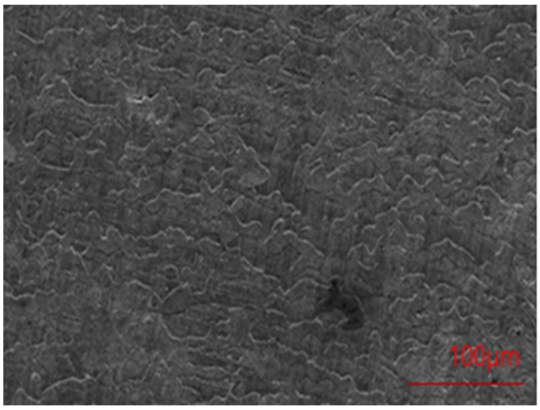

Figure 3: Microstructure of siver alloy added 0.5wt% Nd.

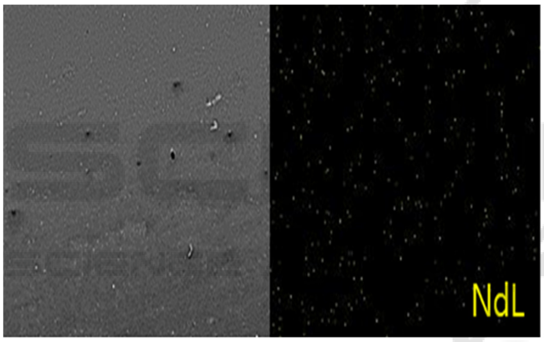

Figure 4: SEM Image with EDS Mapping of silver alloy added 0.5 wt. % Nd.

Table 2: Elemets and wt. % of each elements in silver alloy added 0.5 wt. % Nd.

Element	Wt%
Ok	01.90
Cul	06.73
Ndl	00.61
Agl	92.77

EDS analysis was performed to confirm the addition of Nd. Table 2 shows the quantitative results of the mapping shape in Figure 4. Mapping of the Nd element was performed through EDS to confirm the dispersion of Nd. As a result, Nd was homogeneously distributed and oxidation occurred at high temperature during casting, and oxygen was present, and the same composition as the composition of the synthesized alloy was detected. Based on this, it was confirmed that the alloying was properly performed.

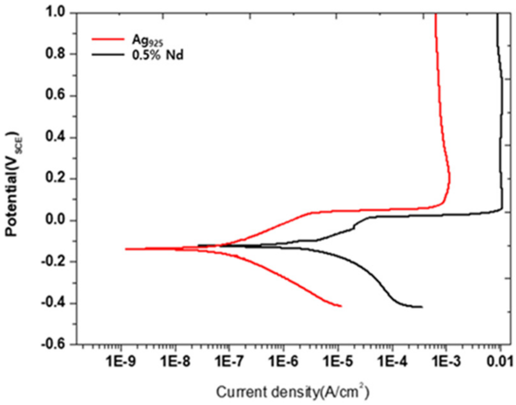

Figure 5: Potentiodynamic polarization curve of silver alloy Ag925 and silver alloy added 0.5 wt% Nd.

Through the electrokinetic polarization experiment, the corrosion resistance of the specimens with Nd and without Nd was compared. In the coincidence polarization test, the corrosion potential represents the potential at the time when corrosion occurs, and through this, it can be confirmed that the corrosion resistance is improved. The results of the comparison are shown in Fig. 5. It was confirmed that the corrosion potential value was improved when 0.5% Nd was added compared to the alloy without the addition of 16mV E(Corr) Nd. Through this, it was confirmed that when Nd was added, Nd improved the corrosion resistance under the atmosphere of Cl ion.

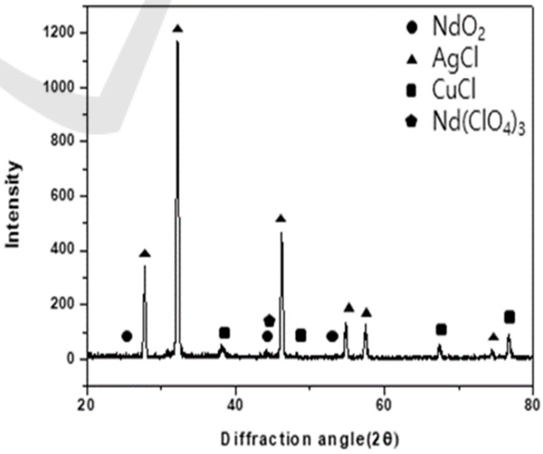

Figure 6: XRD peak after potentiodynamic polarization test of 0.5 wt.% Nd.

Table 3: Phase name and formula for after potentiodynamic polarization test.

Phase name	Formula
Neodymium Oxide	$Nd0_2$
Chlorargyrite	AgCI
Tolbachite	$CuCI_2$
Neodymium Chloratte	$Nd(ClO_4)_3$

Corrosion products generated after electrokinetic polarization were analyzed through XRD, and the results are shown in Figure 6. The results of the XRD analysis of the corrosion products of the specimen to which Nd was added are shown in Table 3. It was confirmed that AgCl, CuCl, NdO2, and Nd(ClO4)3 were generated after the electrokinetic polarization experiment.

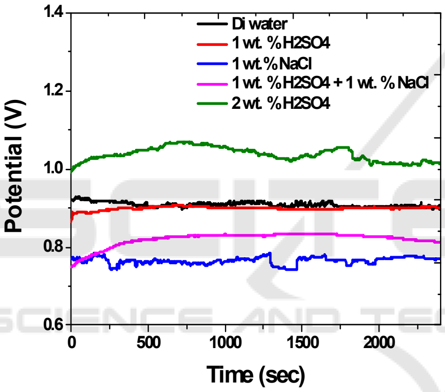

Figure 7: Open circuit potential.

Figure 7 Represents Open circuit potential of each electrolyte. Each electrolyte H2SO4, NaCl, mixture(H2SO4 + NaCl) shows + potentials.

4 CONCLUSIONS

The corrosion resistance and corrosion properties of the conventional silver alloy and the alloy containing Nd added to the silver were compared under Cl atmosphere. To prevent the corrosion of silver, ICCP was connected to evaluate the anticorrosive ability according to voltage, and the electrochemical characteristics according to the electrolyte solution were analyzed, and the following conclusions were drawn.

1) It was confirmed that when 0.5wt% Nd was added, it did not form another secondary phase by bonding with Ag and Cu.
2) As a result of evaluating the polarization potential, the corrosion resistance was improved in the 3.5 wt% NaCl ion atmosphere as Nd was added.
3) When Nd is added, when corrosion occurs in a Cl ion atmosphere, NdO2 is formed on the surface, and it is judged to improve corrosion resistance by first reacting with Cl.
4) ICCP can prevent corrosion of silver by sulfuric acid, and NaCl 1 cm2 with 1.5 voltage.
5) To prevent corrosion of silver, it is necessary to adjust the voltage according to the environment according to the solution.
6) Corrosion of silver can be prevented with ICCP, and contact pressure control according to the environment is required.

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