

## **Twin-Jet Electropolishing of Cast Sterling Silver Alloys Using Perchloric Acid and Potassium Cyanide Solutions**

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### **Abstract**

Twin-jet electropolishing of Ag-4.87 wt%Cu-0.79 wt%Zn-0.09 wt%Si alloy was studied. Two electrolytes, i.e. potassium cyanide solution in distilled water and glycerol-perchloric acid solution in absolute ethanol, were used in the experiments. Effects of parameters including voltage and electrolyte concentration have been studied. Surface of polishing specimens and artifact formed were characterized by light microscopy and electron microscopy. In general, the potassium cyanide solution is a better electrolyte than the glycerol-perchloric acid solution. A more uniform polishing can be obtained from the potassium cyanide solution at the voltage higher than 5 V. Increasing of the potassium cyanide concentration reduced the electrical resistance of the electrolyte and polishing time. The concentration of 150 g KCN/L is recommended. By using the glycerol-perchloric acid solution, artifact as fine silver dendrites was found pronouncingly on the polished specimen. This artifact was considered as a major drawback and its mechanism of formation has been discussed.

**Key words:** Electropolishing, Sterling Silver Alloy, Perchloric Acid, Potassium Cyanide, Transmission Electron Microscopy.

### **Introduction**

Cast Sterling silver alloys are the most commonly used silver-copper alloys in the jewelry industry. According to the international standard, silver content in Sterling silver must be at least 92.5 wt% and the rest (7.5 wt%) is alloying elements. Purer grades of silver are too soft and weak, usually 60-70 HV for standard as-cast Sterling silver alloy. Alloying elements such as Cu are therefore needed to improve mechanical properties, especially strength and hardness. The major drawback of the Ag-Cu alloy is its susceptibility to corrosion, which appears as yellow-brown flecking and gradually becomes a continuous film and darkens the surface. Recently, new Sterling silver alloys with lower Cu content and additional elements such as Zn, Si, Ge, Ir and B were introduced to jewelry manufacturing.<sup>(1-3)</sup> To understand relationship between structure and properties of these Sterling silver alloys and roles of alloying elements, detailed microstructural investigation by transmission electron microscopy (TEM) is essential and good practice in thin-foil

preparation for TEM by twin-jet electropolishing is usually needed.

Silver is a precious metal which is relatively non-active. Therefore, difficulty often arises in twin-jet electropolishing of silver alloys for TEM. Few literatures can be found<sup>(4-6)</sup>, in which two electrolytes, i.e. potassium cyanide solution and glycerol-perchloric acid solution, have been recommended. However, effects of parameters in twin-jet electropolishing have not been described and effects of alloying elements in the silver alloys have not been studied. The aim of this study is therefore to investigate effects of some parameters, i.e. voltage and concentration of electrolytes, and also effects of alloying elements, especially copper, on twin-jet electropolishing of Sterling silver alloy.

### **Materials and Experimental Procedure**

#### **Materials and Method**

A Sterling silver alloy was prepared by casting under argon protection atmosphere. Its

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chemical composition was determined by inductively couple plasma (ICP) technique as given in Table 1. A Struer Tenupol-III twin-jet electropolishing machine was used for thin-foil preparation.

Two experiments were performed. In the experiment A (Table 2), two electrolytes were used for twin-jet electropolishing including (i) 150 g/L potassium cyanide solution in distilled water (KCN) and (ii) 10 vol% glycerol–20 vol% perchloric acid solution in absolute ethanol (GPE). The voltage was varied in the range of 1–9 V, while the electrolyte flow rate (75 ml/min for KCN and 95 ml/min for GPE) and the sensitivity of the photodiode were kept constant. In the experiment B (Table 3), only KCN was used as the electrolyte and its concentration was varied in the range of 50–200 g KCN/L. Details of mA and polishing time until penetration occurred were given in both tables.

General microstructure of the alloy was studied by a JEOL 5910LV scanning electron microscopy equipped with an Oxford-Inca spectrometer for energy dispersive x-ray spectroscopy (EDS). Surfaces of thin-foils were investigated by an Olympus BX60M light microscopy. Areas around the holes formed in thin foils by twin-jet electropolishing were studied by the JEOL 5910LV scanning electron microscope operated at 15 kV and a JEOL JEM2010 operated at 200 kV.

**Table 1.** Chemical composition of the Sterling silver alloy used in this work.

Elements	Cu	Zn	Si	Ag
wt%	4.78	0.79	0.09	Bal.

**Table 2.** Details of parameters in the experiment A.

Electrolytes	Voltage (V)	Current (mA)	Polishing Time (s)
KCN (150 g/L)	1	10	132
	3	43	35
	5	130	10
	7	157	7
	9	182	4
GPE	1	NP	NP
	3	43	129
	5	52	76
	7	62	56
	9	58	24

NP = No penetration occurred.

**Table 3.** Details of parameters in the experiment B.

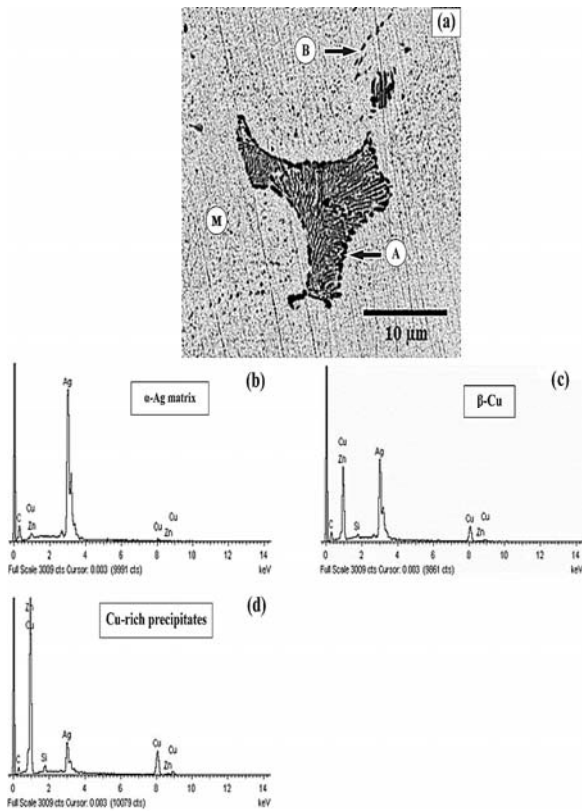
KCN (g/L)	Voltage (V)	Current (mA)	Polishing Time (s)
50	1	6	182
	3	42	84
	5	74	42
	7	92	32
	9	100	32
150	1	10	132
	3	43	35
	5	130	10
	7	157	7
	9	182	4
200	1	8	64
	3	20	22
	5	120	6
	7	146	5
	9	240	4

## Results and Discussion

### General Microstructure of the Alloy

Figure 1(a) is a backscattered electron image in scanning electron microscopy (SEM-BEI) showing general microstructure of the Sterling silver alloy used in this work. The microstructure consists of primary  $\alpha$ -Ag (as dendrites or grains) and colonies of typical lamellar eutectic  $\alpha$ -Ag and  $\beta$ -Cu as identified by SEM-EDS in Figures 1(b) and (c). Cu-rich precipitates as indicated by SEM-EDS in Figures 1(d) were also observed at grain boundaries of primary  $\alpha$ -Ag. These eutectic structure and precipitates occurred due to segregation of alloying elements to edges of dendrites during solidification.

*Twin-Jet Electropolishing of Cast Sterling Silver Alloys Using Perchloric Acid and Potassium Cyanide Solutions*



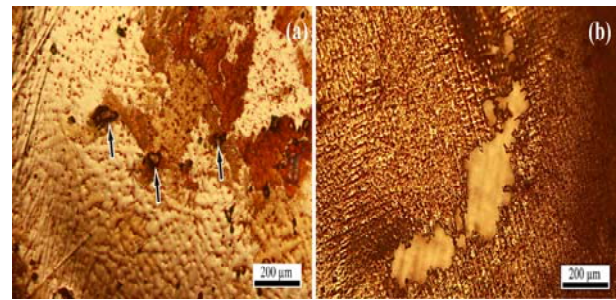
**Figure 1.** (a) SEM-BEI shows general microstructure of the 4.87 wt%Cu-0.79 wt%Zn-0.09 wt%Si silver alloy, (b-d) EDS spectra from matrix (M),  $\beta$ -Cu (A) and Cu-rich precipitates (B), respectively

### Characteristics of Polishing Surface

Light micrographs in Figure 2 show examples of thin-foil surfaces after twin-jet electropolishing using KCN (Figure 2(a)) and GPE (Figure 2(b)) as electrolytes.

In general, a more uniform polishing can be obtained from KCN. Dendrites of  $\alpha$ -Ag were partly revealed. Penetration was faster at the vicinity near grain boundaries or eutectic structure, where holes were finally formed (e.g. at arrows in (Figure 2(a)). This can be an effect of alloying elements, mainly Cu, which segregated during casting of the Sterling silver alloy and enhanced polishing rate at grain boundaries or eutectic structure. The half-cell potentials of possible reactions occurred during twin-jet electropolishing is given in Table 4, taken from Milazzo<sup>(7)</sup> and the standard cell potentials  $E^{\circ}_{cell}$  for possible redox reactions during twin-jet electropolishing can be calculated as given in Table 5. In the case of KCN, redox

reactions (1) to (5) in Table 5 are relevant. The redox reaction (3) requires less external potential than the redox reaction (1), hence, regardless of kinetic effects, oxidation of  $\text{Cu} \rightarrow [\text{Cu}(\text{CN})_2]^-$  is thermodynamically more favourable than  $\text{Ag} \rightarrow [\text{Ag}(\text{CN})_2]^-$ . This can explain characteristics of the polished surface shown in (Figure 2(a)). Even though the redox reaction (2) may also take place, but the external potential required is slightly lower than that of the redox reaction (3).



**Figure 2.** Light micrographs show surface around holes in TEM thin foils of the Ag-4.87 wt%Cu-0.79 wt%Zn-0.09 wt%Si alloy prepared by twin-jet electropolishing using KCN 150g/L and GPE: (a) KCN 5 Volt and (b) GPE 3 Volt.

**Table 4.** Standard half-cell potentials of possible reactions occurred during twin-jet electropolishing.

Half-cell reactions	$E^{\circ}$ , V
$2\text{Ag}_{(s)} \rightarrow 2\text{Ag}^+_{(aq)} + 2e^-$	+ 0.80
$2\text{Cu}_{(s)} \rightarrow 2\text{Cu}^+_{(aq)} + 2e^-$	+ 0.52
$\text{Cu}_{(s)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2e^-$	+ 0.34
$2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_{2(g)}$	0.00
$2\text{Ag}_{(s)} + 4\text{CN}^-_{(aq)} \rightarrow 2[\text{Ag}(\text{CN})_2]^-$	-0.31
$2\text{Cu}_{(s)} + 4\text{CN}^-_{(aq)} \rightarrow 2[\text{Cu}(\text{CN})_2]^-$	-0.43
$2\text{Ag}_{(s)} + 6\text{CN}^-_{(aq)} \rightarrow 2[\text{Ag}(\text{CN})_3]^{2-}$	-0.51
$\text{H}_{2(g)} + 2\text{OH}^-_{(aq)} \rightarrow 2\text{H}_2\text{O} + 2e^-$	-0.83

Note: Data in this table were taken from Milazzo [7].

**Table 5.** Standard cell potentials for possible redox reactions during twin-jet electropolishing.

Redox Reactions	$E^0_{\text{cell}}$ , V
<b>KCN solution</b>	
(1) $2\text{Ag}_{(s)} + 4\text{CN}^-_{(aq)} + 2\text{H}_2\text{O} \rightarrow 2[\text{Ag}(\text{CN})_2]^-_{(aq)} + \text{H}_{2(g)} + 2\text{OH}^-_{(aq)}$	-0.52
(2) $2\text{Ag}_{(s)} + 6\text{CN}^-_{(aq)} + 2\text{H}_2\text{O} \rightarrow 2[\text{Ag}(\text{CN})_3]^{2-}_{(aq)} + \text{H}_{2(g)} + 2\text{OH}^-_{(aq)}$	-0.32
(3) $2\text{Cu}_{(s)} + 4\text{CN}^-_{(aq)} + 2\text{H}_2\text{O} \rightarrow 2[\text{Cu}(\text{CN})_2]^-_{(aq)} + \text{H}_{2(g)} + 2\text{OH}^-_{(aq)}$	-0.40
(4) $2\text{Cu}_{(s)} + 2[\text{Ag}(\text{CN})_2]^-_{(aq)} \rightarrow 2[\text{Cu}(\text{CN})_2]^-_{(aq)} + 2\text{Ag}_{(s)}$	-0.12
(5) $2\text{Cu}_{(s)} + 2[\text{Ag}(\text{CN})_3]^{2-}_{(aq)} \rightarrow 2[\text{Cu}(\text{CN})_2]^-_{(aq)} + 2\text{CN}^-_{(aq)} + 2\text{Ag}_{(s)}$	+0.08
<b>GPE solution</b>	
(6) $2\text{Ag}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow 2\text{Ag}^+_{(aq)} + \text{H}_{2(g)}$	-0.80
(7) $2\text{Cu}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow 2\text{Cu}^+_{(aq)} + \text{H}_{2(g)}$	-0.52
(8) $\text{Cu}_{(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Cu}^{2+}_{(aq)} + \text{H}_{2(g)}$	-0.34
(9) $\text{Cu}_{(s)} + 2\text{Ag}^+_{(aq)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2\text{Ag}_{(aq)}$	+0.46
(10) $2\text{Cu}_{(s)} + 2\text{Ag}^+_{(aq)} \rightarrow 2\text{Cu}^+_{(aq)} + 2\text{Ag}_{(s)}$	+0.28

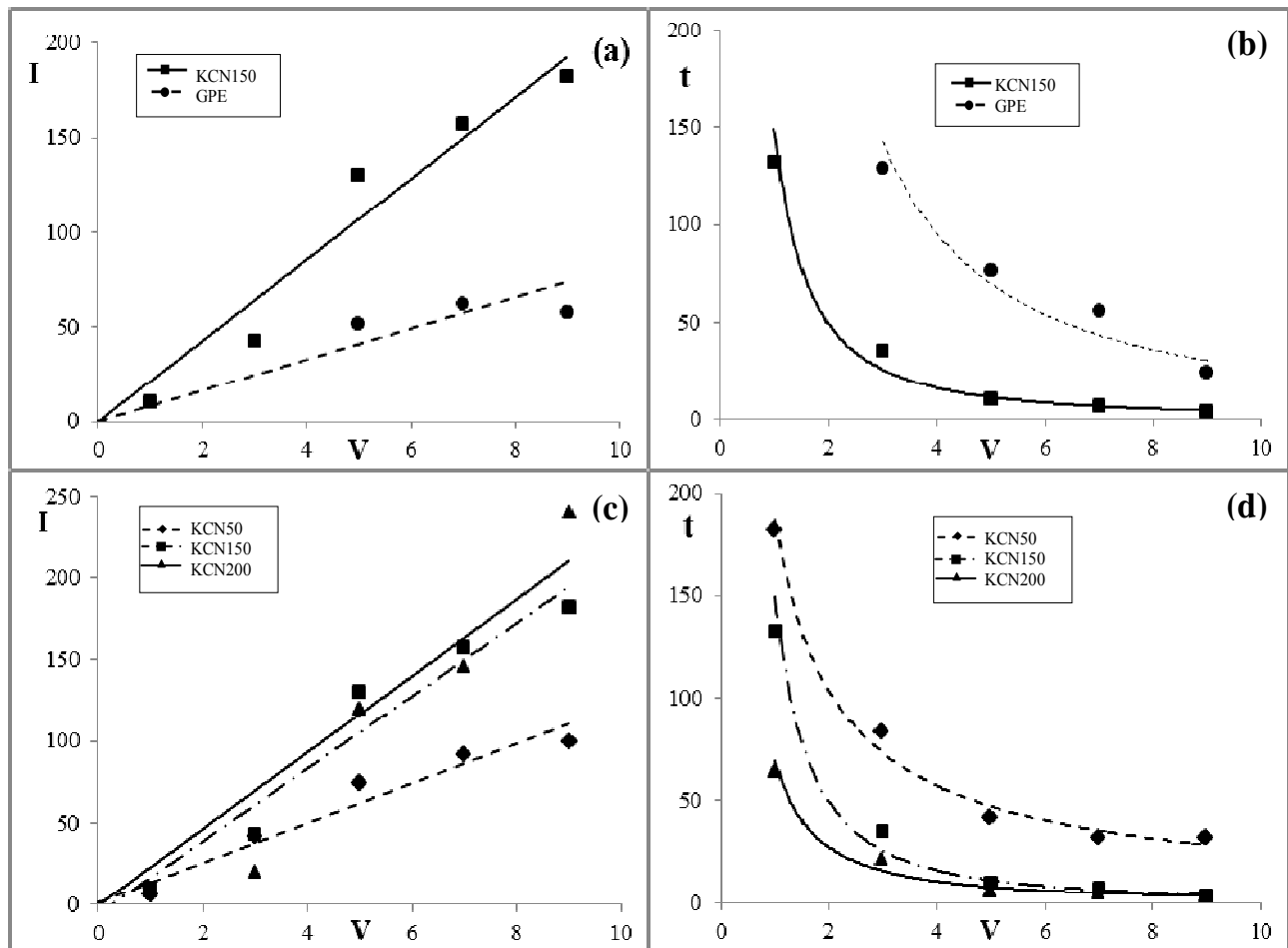
Note: Data in this table were calculated from the data in Table 4.

In the case of GPE, the effect of segregation of alloying elements discussed above is more pronounced so that polishing was preferential on the areas between dendritic arms and the dendritic structure of  $\alpha$ -Ag was clearly revealed in (Figure 2(b)). In this case, redox reactions (6) to (10) in Table 5 are relevant and the redox reaction (7) requires less external potential than the redox reaction (6). Again, regardless of kinetic effects, oxidation of  $\text{Cu} \rightarrow \text{Cu}^+$  is thermodynamically more favourable than  $\text{Ag} \rightarrow \text{Ag}^+$ . This can also explain characteristics of the polished surface shown in Figure 2(b). Moreover, it has been noticed that current density was concentrated at the electrical contact of the specimen holder, resulting in a formation of large holes in (Figure 2(b)) as compared to those in (Figure 2(a)). Therefore, KCN is considered as a better electrolyte for twin-jet electropolishing of the Sterling silver alloy than GPE.

### *Effects of Voltage and KCN Concentration*

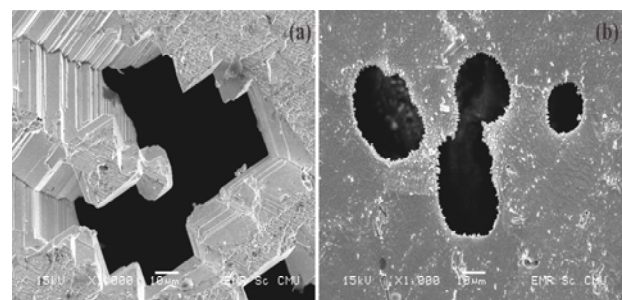
Plots of current (I) and polishing time (t) versus voltage (V) during twin-jet electropolishing in both experiments are given in Figure 3. As  $V = IR$ , plots of I versus V can be expressed by linear equations and the slope is correspond to  $1/R$ , while plots of t versus V can be expressed by power equations,  $t = aV^b$ , where a and b are parameters. From (Figures 3(a-b)), resistance of the 150 g KCN/L solution is about 2.5 times lower than that of the GPE solution and polishing required less time. Effects of KCN concentration are illustrated in (Figures 3(c-d)), in which the resistance of the KCN electrolyte decreased as KCN concentration increased, resulting in a decrease in polishing time.

*Twin-Jet Electropolishing of Cast Sterling Silver Alloys Using Perchloric Acid and Potassium Cyanide Solutions*



**Figure 3.** Plots of current (I) and polishing time (t) versus voltage (V): (a-b) experiment A, and (c-d) experiment B.

Figures 4(a) and 4(b) are examples of secondary electron images in scanning electron microscopy (SEM-SEIs) of holes formed by twin-jet electropolishing using KCN and GPE, respectively. At relatively low voltage, polishing by KCN partly took place on specific crystalline planes, leading to faceted pits. This is considered as a drawback since the area around pitting holes would not be thin enough for transmission electron microscopy. Increasing the voltage above about 5 V can eliminate this problem and typical round holes can be obtained with thin areas. Facetted pits were not observed in the case of GPE, but large amount of artifact was found on the specimen, especially at relatively high voltage, as shown in Figure 4(b). Detailed study on nature of this artifact will be discussed in the following section.



**Figure 4.** SEM-SEIs show characteristics of holes formed by twin-jet electropolishing: (a) facetted pits by KCN 200g/Lat 3 V, and (b) round holes with artifact by GPE at 9 V.

#### *Artifact Formed on Thin Foils*

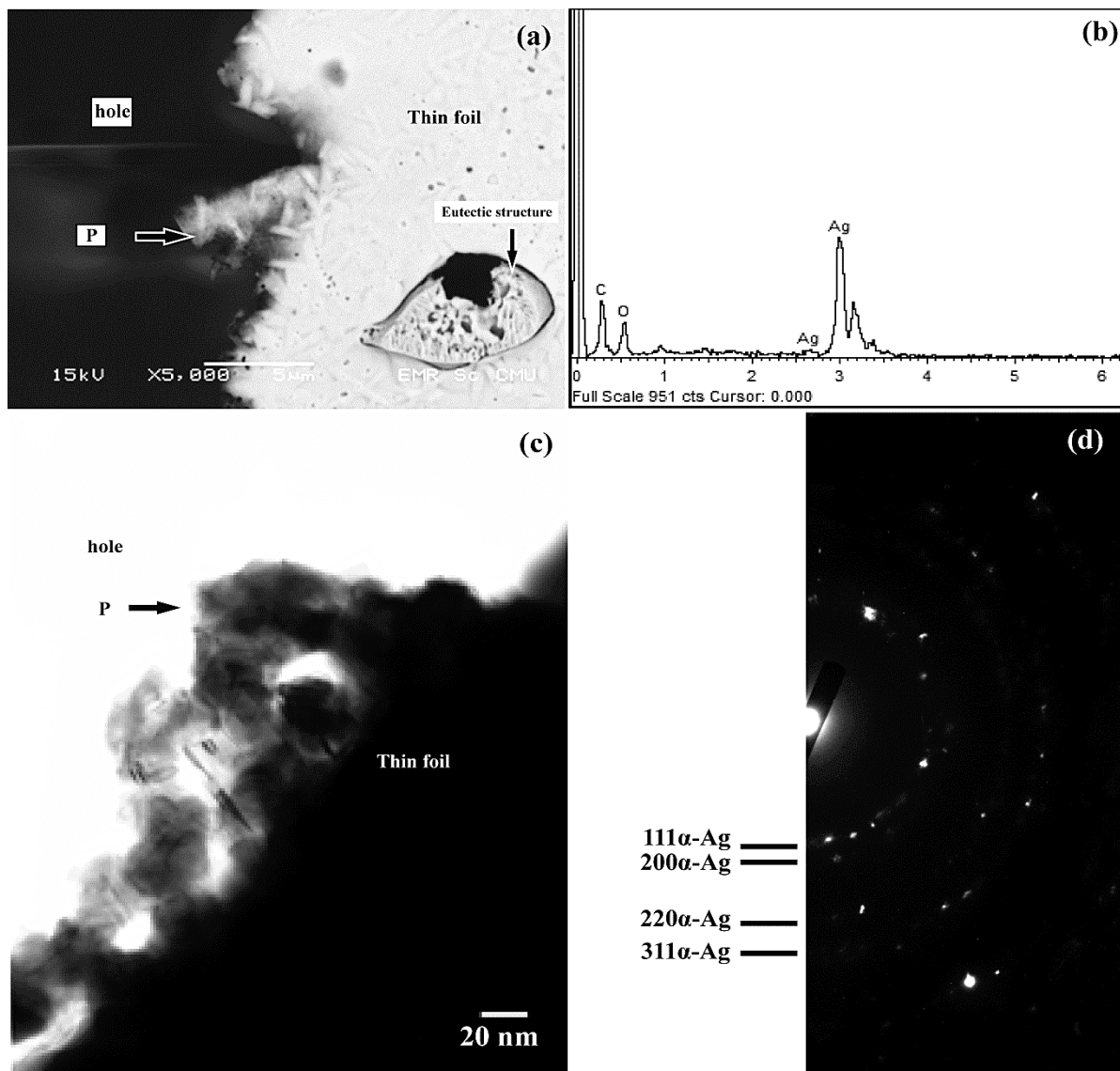
Characteristics of artifact formed around the holes in thin foils after twin-jet electropolishing



using KCN and GPE are shown in Figures 5 and 6, respectively.

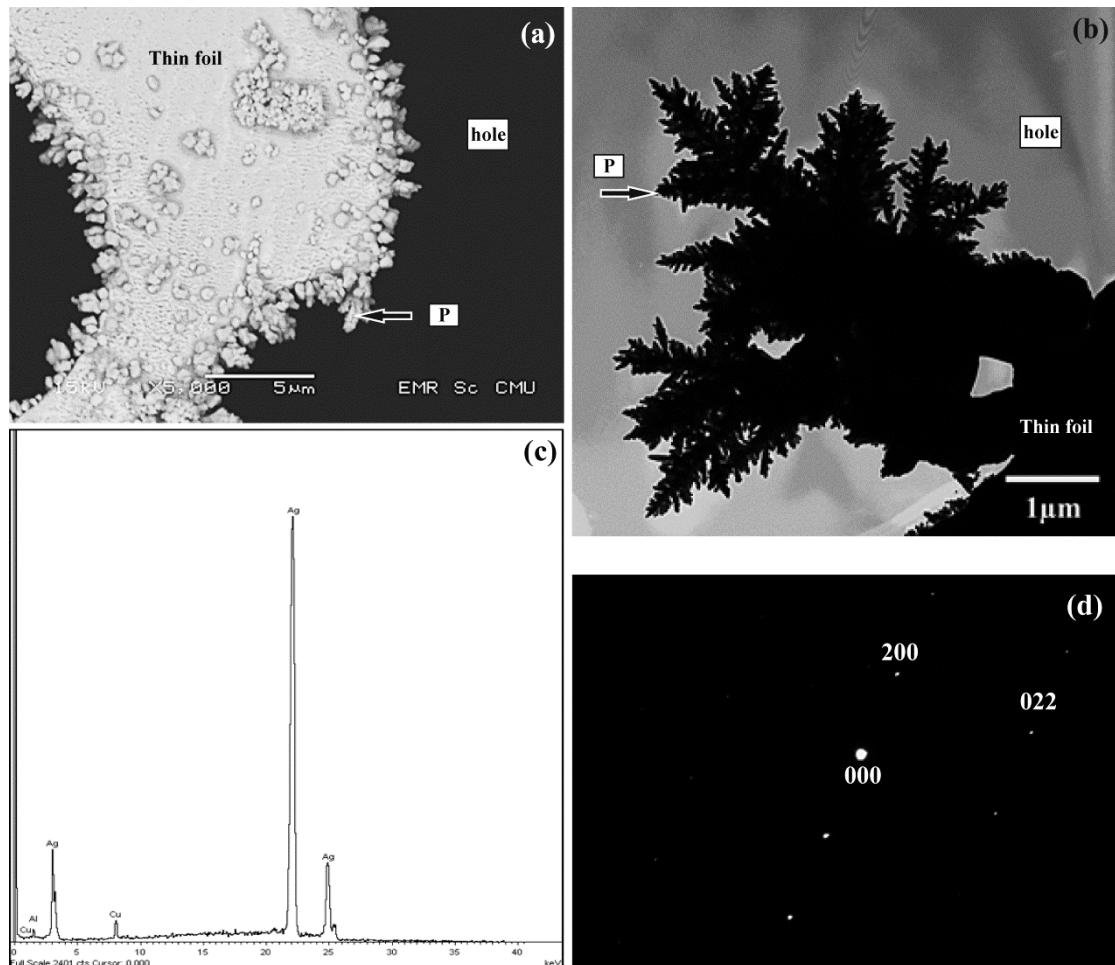
In the case of KCN, platelet crystals were observed only in some areas (e.g. marked 'P' in Figure 5(a)) and identified as  $\alpha$ -silver by TEM-EDS (Figures 5(b-c)) and selected area diffraction pattern (SADP) in TEM (Figure 5(d)). However, this is not pronounced and most of the thin areas are free from this artifact. On the other hand, in the case of GPE, dendritic crystals were observed all over the thin foils (Figure 6(a)) and identified as  $\alpha$ -silver dendrites by TEM-EDS (Figures 6(b-c)) and TEM-SADP (Figure 6(d)). The formation of these silver dendrites can be explained by considering the

redox reactions (9) and (10) in Table 5. Oxidation of  $\text{Cu} \rightarrow \text{Cu}^+/\text{Cu}^{2+}$  can be a galvanic counterpart for reduction of  $\text{Ag}^+ \rightarrow \text{Ag}$  when GPE is used. At the anode during twin-jet electropolishing, redeposition of  $\text{Ag}_{(s)}$  from GPE electrolyte as  $\alpha$ -silver dendrites on thin foils is then possible. This is not the case for KCN, since the redox reactions (4) and (5) in the environment containing cyanide ions are not thermodynamically favourable. Regarding these artifacts, KCN can be considered as a better electrolyte than GPE for twin-jet electropolishing.



**Figure 5.** Characteristics of the artifact formed around the holes after twin-jet electropolishing using KCN 150 g/L: (a) SEM-BEI, (b) BF-TEM image of platelet crystals, (c) TEM-EDS spectrum from the platelet crystal marked 'P' in (b), and (d) Corresponding SADP from the platelet crystals, which can be indexed as  $\alpha$ -Ag.

*Twin-Jet Electropolishing of Cast Sterling Silver Alloys Using Perchloric Acid and Potassium Cyanide Solutions*



**Figure 6.** Characteristics of the artifact formed around the holes after twin-jet electropolishing using GPE: (a) SEM-BEI, (b) BF-TEM image of dendritic crystals, (c) TEM-EDS spectrum from the dendritic crystal marked 'P' in (b), and (d) Corresponding SADP from the dendritic crystals, which can be indexed as  $\alpha$ -Ag.

## Conclusions

(i) The microstructure of the Ag-4.87 wt%Cu 0.79 wt%Zn-0.09 wt%Si alloy consists of primary  $\alpha$ -Ag dendrites and a typical eutectic lamellar structure of eutectic  $\alpha$ -Ag and Cu-rich,  $\beta$ -phase.

(ii) A more uniform twin-jet electropolishing can be obtained from KCN. Penetration was faster at the vicinity near grain boundaries or eutectic structure, which can be explained by thermodynamic preference of oxidation of alloying elements, especially Cu, segregated to grain boundaries. The electrical resistant of the 150 g KCN/L is about 2.5 times lower than that of GPE. Increasing KCN concentration decreased the electrical resistance and polishing time.

(iii) At relatively low voltage, Twin-jet electropolishing by KCN took place on specific

crystalline planes, leading to faceted pits. To generate thin areas for TEM, the voltage should be less than about 5 V.

(iv) The artifact, characterized as small Ag dendrites, pronouncingly formed by galvanic effects on thin areas when GPE was used. KCN can therefore be considered as a better electrolyte for twin-jet electropolishing of Sterling silver alloy.

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## References

1. Fischer-Buehner, J. (2003). An update on hardening of sterling silver by heat treatment. *Santa F* **19** : 29-48.
2. Davitz, D. (1999). Silver colored alloy with low percentage copper *United State. Pat.* No. 5882441.
3. Nisaratanaporn, S. and Nisaratanaporn, E. (2003). The Anti-tarnishing microstructure analysis and mechanical properties of sterling silver with silicon additive. *J. Met. Mater. Miner.* **12(2)** : 13-18.
4. Petzow, G. (1999). *Preparation and etching recipes for metallic materials Metallographic Etching.* Materials Park, OH : ASM International : 53-57.
5. Goodhew, P. J. (1985). Thin Foil Preparation for Electron Microscopy. In : *Practical Methods in Electron Microscopy.* Amsterdam : Elsevier Science Pub : 51-94.
6. Thompson-Russell, K.C., and Edington, J.W. (1974) Tables of Specimen Preparation Techniques. In : *Electron Microscope Specimen Preparation Techniques in Materials Science.* London : Macmillan Press : 1- 87.
7. Milazzo, G. (1963). Galvanic cells. In : *Electrochemistry: Galvanic cells.* London : Newnes :156-172.