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# The Effects of Depositing Sn-Ag-Cu-S Systems at Different Temperatures on Silver Substrates

Pathra Srisukho[1,a] and Kageeporn Wongpreedee[1,b]

[1]Gems & Jewelry Programs, Department of General Science, Faculty of Science,
Srinakharinwirot University, Thailand

[a]pathra.sri@gmail.com, [b]kageeporn@gmail.com

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**Abstract.** Niello bars contain Lead which prohibits by laws and danger to environment. This research was to study the effects of temperatures which a black amalgam of lead-free niello bar alloys was filled in carved grooves of 95wt%Ag-5wt%Cu and 99.99wt%Ag substrates at 400°C, 500°C, 600°C and 700°C. Three compositions of lead-free niello bar alloys were selected in this research. The characterizations of microstructure, interface layers, and porosities of lead-free niello bar alloys after applying were reported. The results showed that all three compositions contain six compounds of CuAgS, Ag, $Cu_2S$, $Sn_2S_3$, SnS and $Cu_4SnS_4$. After applying lead-free niello bar alloys on the substrates, it showed that composition #2 on the 95wt%Ag-5wt%Cu substrates was matched to the best condition of temperature at 600°C giving lowest porosities.

## Introduction

The niello bar is raw materials to make nielloware. Nilloware is silver alloy handcrafts having grooves deposited black niello bars into them. The history of nielloware has been in existences for centuries revealing mostly in Europe and Asia, Portuguese, India, and Thailand [1]. It is had been known elsewhere that the compositions of niello bar were made of Pb, Ag, Cu, and S compounds [2,3]. When the niello bar is melted, it brings about the lead toxic occurrences contaminating in the production processes. The prohibition and regulations, especially in Europe and United State, amount of Lead contaminations in the products should not exceed 600 ppm [4,5].

Recently, K.Wongpreedee and et.al. were firstly innovated various compositions of lead-free niello- bar alloys of Sn-Ag-Cu-S system in 2011[6]. It is commercialized now under the name of Nielli Inlay. Then, P.Srisukho had been studied microstructures and segregations of lead-free niello bar alloys [7]. The microstructures were shown the ratio eutectic-like and needle-like with different compositions. It also displayed the Cu-Sn-S compounds of eutectic-like and Sn-S compounds of needle-like. In 2012, K.Wongpreedee and et.al. comparatively investigated microstructure and segregations of lead and lead-free niello bar alloys at various sources and compositions [8]. The compound of CuAgS was the only compound showing on both alloys. It is also showed that lead-free niello bar alloys was harder than lead niello bar alloys. Moreover, K.Wongpreedee and et.al. had studied the interfaces of lead-free niello bar alloys on brass-substrates[9]. It showed the white spots and undesirable physical properties of nielloware due to the intermetallic of Cu-Sn at interfaces of lead-free niello bar alloys and brass substrates.

In this work, we studied the relations of compounds and microstructure of lead-free niello bar alloys at various compositions. It was also investigated the effects of different depositing temperatures of lead-free niello bar alloys into grooves by characterizing the interfaces and porosities.

## Experimental Procedures

Lead-free niello bar alloys were prepared from pure metals of tin, copper, silver and sulfur at various 3 compositions as shown in Table 1. All alloys were melted in reducing atmosphere by gas $H_2$ protective at 1,100°C. After that, the alloys were poured into ingot with dimensions of

$0.85\times7.0\times0.85 cm^3$ and $1.5\times1.5\times x1.0 cm^3$ controlled the heat direction of solidification of alloys from bottom to the top. The compositions were then studied microstructures and crystalline structure.

Table 1. Compositions of lead-free niello bar alloys

| **Lead-free niello bar alloys** | **Sn** (wt%) | **Ag** (wt%) | **Cu** (wt%) | **S** (wt%) |
|---|---|---|---|---|
| 1 | 32 | 14 | 34 | 20 |
| 2 | 38 | 11 | 31 | 20 |
| 3 | 43 | 8 | 29 | 20 |

The first part of experiments was carried on the microstructure and crystallography relations to understand all compounds at various compositions. The compositions were characterized crystallography by X-ray diffraction (XRD: Bruker D8 ADVANCE). Then, the compositions were comparatively investigated microstructures at each compound using backscatter modes and qualitatively analyzed the compositional contrasts of each phase using Energy Dispersive spectroscopy (EDS) equipped in scanning electron microscope (SEM: Jeol-JSM-5410LV) with a voltage of 20 keV.

The second part was to study porosities and interfaces of lead-free niello bar alloys on silver base substrates. Those properties are important to understand as commercial products. Two compositions of silver base substrates were selected at 99.99wt%Ag and 95wt%Ag-5wt%Cu to apply all three compositions of Lead-free niello bar alloys as indicated in Table 1. The substrate prototype was prepared by CNC machine with a dimension of 1.5×1.0×0.12 cm3 with a groove of 1×0.2×0.7 cm3. All substrate samples were reproduced by lost wax casting techniques. The silver base substrates were heated to 400◦C, 500◦C, 600◦C and 700◦C. Lead-free niello bar alloys were applied by re-melting them into the grooves. After applied the heat, the compositions were cooled in the air for 30 seconds and quench in water.

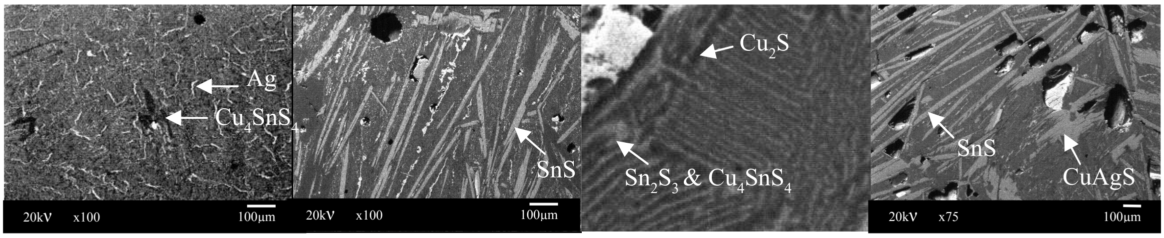
Once, the lead-free niello bar alloys were re-melted into the grooves of silver substrates. All samples were characterized porosities by taking the selected area images using optical microscopes. The images were characterized by using Image J program to analyze porosities. The interface layers between lead-free niello alloys and silver substrates were analyzed by EDS of the 2D line scan mode equipped in scanning electron microscope (SEM) to obtain the thickness of diffusion interfaces. The crack surfaces would observe the fractrography by high depth of fields of SEM images.

## Results and discussion

### Crystal structure compounds and microstructure relations

Sn, Ag, Cu and S were mixed at various compositions of lead-free niello bar alloys and characterized by XRD obtaining the compounds of CuAgS, Ag, $Cu_2S$, $Sn_2S_3$, SnS and $Cu_4SnS_4$. As compared within six compounds, $Cu_2S$ is a desirable compound since it is a cubic system with a= 5.63°A and it is the only one giving the results of a black color [10]. It is noted that $Sn_2S_3$, SnS and $Cu_4SnS_4$ are orthorhombic with big size of unit cell comparing to the rest of three compounds. The other compounds gave grayish-blue colors of CuAgS, brown color of SnS, and silver colors of Ag [10].

The basic understanding of microstructures and crystallography relations are guided to select an appropriated composition to use for commercial products. The most desirable combination alloy was compositions #2 obtaining highest amount of $Cu_2S$ and less segregations of Ag. Fig. 1(b) showed needle-like structures of SnS. In zooming area, it was indicated the combinations of eutectic-like structure consisting of $Cu_2S$ (black areas) with the lamellar-like of $Sn_2S_3$ and $Cu_4SnS_4$ (grey areas). In Fig. 1(a), SEM images of compositions# 1 showed Ag-phase segregating in the matrix. It was due to the excess amounts of Ag. It was also showed irregular shapes of $Cu_4SnS_4$. It might be because of a relative big unit cell of $Cu_4SnS_4$ which hardly combines well with others. In Fig. 1(d), lead-free niello bar alloys of compositions #3 had even highest amounts of needle-like SnS compounds because of increasing the excess amounts of Sn. It was also shown that the irregular shapes of CuAgS compounds were scattered in the matrix. The needle-like microstructures can be explained that there is an incoherent mismatch atomic size of an orthorhombic system with a large unit cell and $Cu_2S$ cubic matrixes.



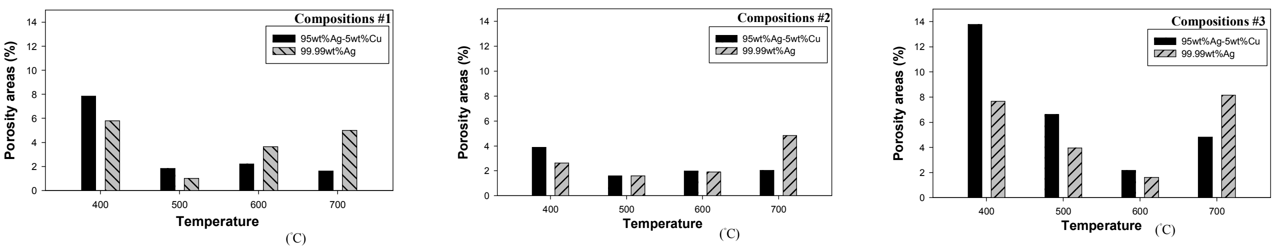

(a) (b) (c) (d)

Figures 1. The microstructures of Lead-free niello bar alloys by SEM and indicating components (a) compositions#1, (b,c) compositions#2, (d) compositions#3

## Porosity

There are two aspects of porosity observations. The first aspect was to obtain less porosity at a certain temperature of depositing lead-free niello bar alloys into the grooves. The later aspect was to observe amount of porosities depositing lead-free niello bar alloys into two kinds of 99.99 wt%Ag substrates and 95wt%Ag-5wt%Cu substrates.

In fig. 2(b), compositions #2 represented minimized amounts of porosities comparing to others. This result was correlated to the previous experiment [7] that compositions #2 gave the best results. It was indicated that the depositing temperature of 600°C was suitable. It can be explained that ratio combinations of $Cu_2S$ matrix and SnS and $Sn_2S_3$ needle-like were suited. Some certain amounts of needle-like would probably allow an appropriated solidification of $Cu_2S$ to make less porosities. The later aspect was relating to substrate materials. It was conclude that Cu mixing in Ag substrate of 95wt%Ag-5wt%Cu substrates played an important role of porosities. At low temperature depositing (400°C-500°C), it was indicated high amounts of porosities of 95wt%Ag-5wt%Cu substrates comparing to pure silver bases especially in composition#3. This might be because of high amount of Sn in lead-free niello bar alloys which enhanced the migration of Sn to Cu based matrix forming intermetallic which will explain in a latter session.



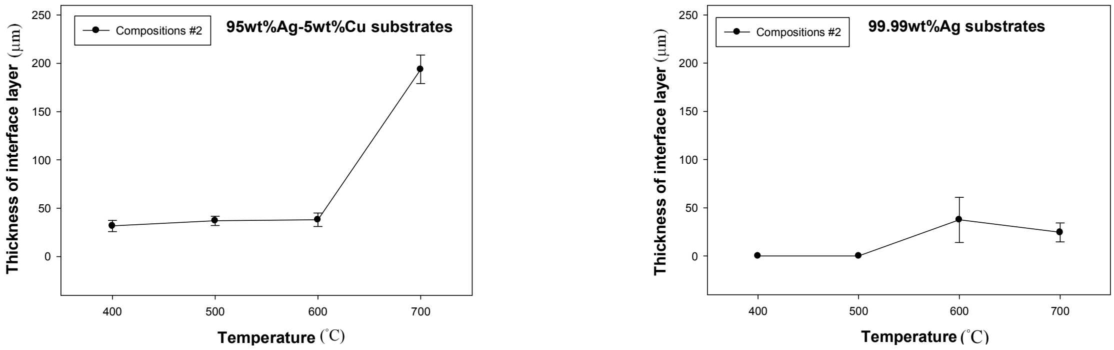

(a) (b) (c)

Figures 2. Average porosity areas (%) of 3 composition a) compositions 1, b) compositions 2, c) compositions# 3 on the 99.99wt%Ag substrates and 95wt%Ag-5wt%Cu substrates at temperature of 400◦C, 500◦C, 600◦C and 700◦C.

## Interface and fractrography

Fig. 3 shows the thickness of interface layers at 400°C-700°C with two types of base metals. It was obviously shown that 95wt%Ag-5wt%Cu substrates gave thicker interface of CuSnAg compounds than 99.99wt%Ag substrates. Moreover, the interface at 700 °C represented the thickest layers especially in 95wt%Ag-5wt%Cu substrates. The microstructures revealed the migration of elements causing the sinusoidal-planar interfaces in temperatures of 500°C, 600°C, 700°C on 95wt%Ag-5wt%Cu substrates as shown in Fig. 4 (b-d). It confirmed the results of migration of Sn-Cu preferred intermetallic bond at the interface [9] existing in higher amount of Cu base substrates.

Fig. 5 shows the fractrography of all lead-free niello bar alloys. It showed the brittleness properties of alloys. It is noted that temperatures of depositing on different based alloys gave the same fractrography results.




(a) (b)

Figures 3. Relationship between thickness of interface layers (µm) of compositions# 2 at temperatures of 400◦C, 500◦C, 600◦C and 700◦C in a) 95wt%Ag-5wt%Cu substrates, b) 99.99wt% Ag substrates

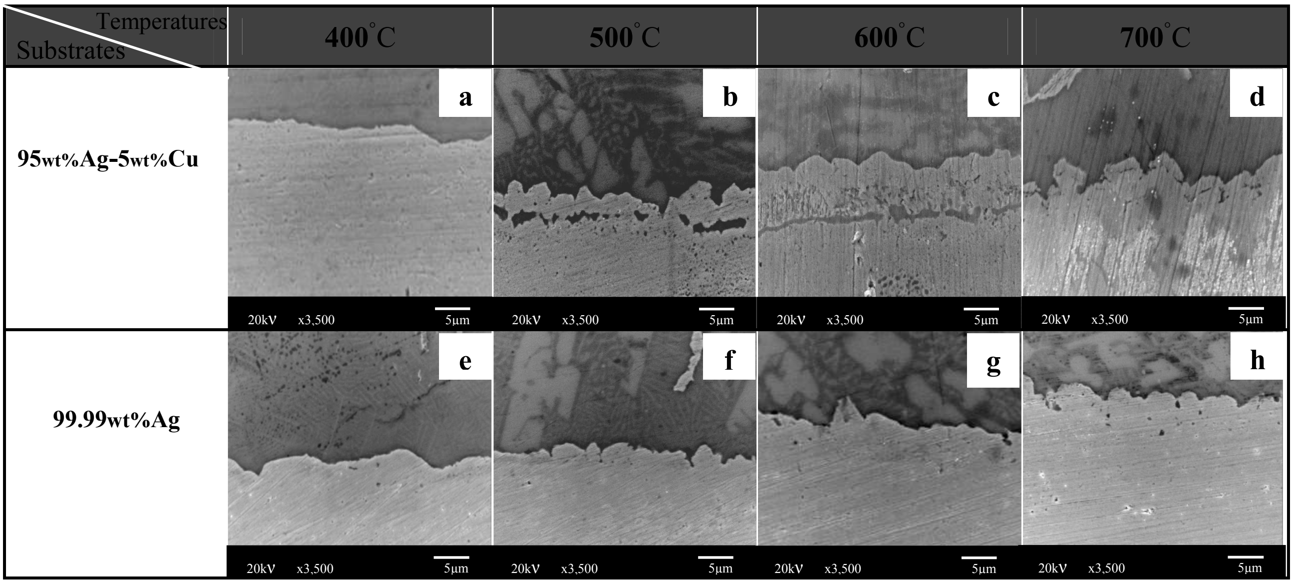
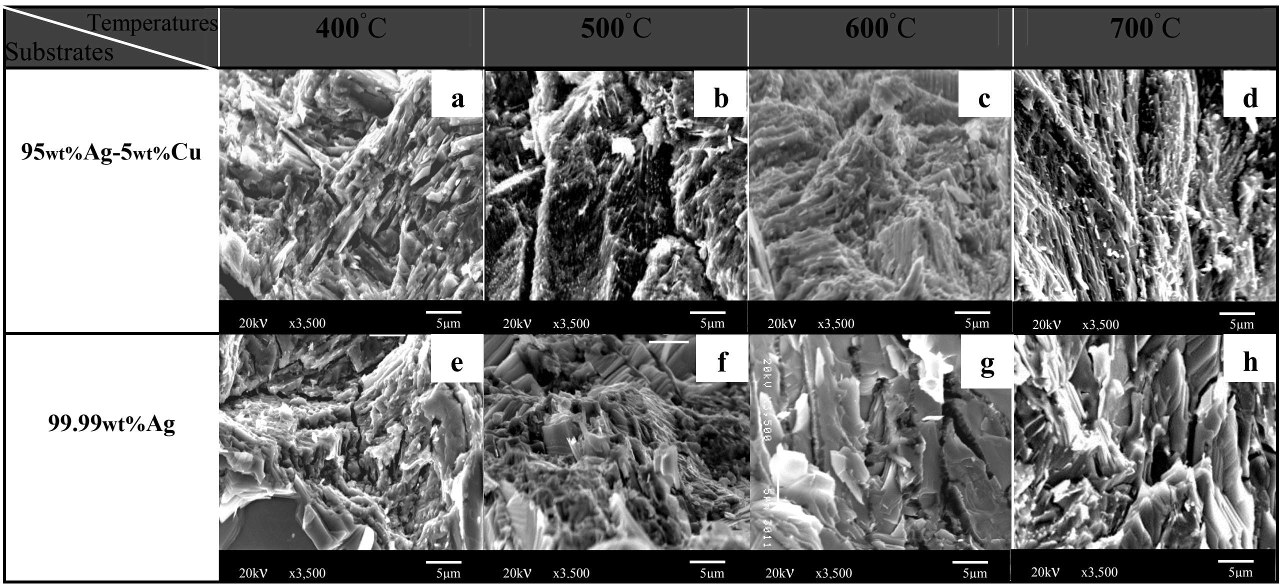



Figure 4. The microstructure of cross-sectional of compositions# 2 on silver alloy (a-d) 95wt%Ag-5wt%Cu substrates, (e-h) 99.99wt%Ag substrates at different temperatures characterized by SEM




Figures 5. Fractography by SEM of the compositions# 2 of lead-free niello bar alloys at 400◦C, 500◦C, 600◦C and 700◦C in (a-d) 95wt%Ag-5wt%Cu substrates, (e-h) 99.99wt%Ag substrates

**Conclusions**

The basic understanding of microstructures, physical properties of porosities and interface, crystallography relations are guided to select an appropriated composition to use as a commercial product giving compositions#2 alloys is most desirable combination. The discover can be concluded that:

1) Lead-free niello bar alloys consists of various compounds which are CuAgS, Ag, $Cu_2S$, $Sn_2S_3$, SnS and $Cu_4SnS_4$. $Cu_2S$ is the most desirable compound.
2) Lead-free niello bar alloys compositions #2 has the least porosities on pure silver substrates.
3) The interface layers of 95wt%Ag-5wt%Cu substrates displays thicker interface layers than pure silver.
4) The cracks of lead-free niello bar on 95wt%Ag-5wt%Cu substrates represents the brittle properties.

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