

The Metallurgy Evolution of Thai Nielloware from Lead to Lead Free Niello bars as a Commercial Export Product

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Extended Abstract

Extended Abstract Nielloware is an asset of art-craft Thai wisdom products[1]. The nielloware is made by filling in its groove and texture with black materials called niello bars. Traditional niello bars contain a lead element which is a toxic substance known to be harmful to human health and environment. It has not yet studied the metallurgical aspects of niello bars from various sources. This research present a collection of research investigating and comparing metallurgy aspects of lead and lead free niello bars. Lead niello bars were investigated and compared the composition, microstructure and crystallography from various sources. The Scanning Electron Microscopy (SEM) results show dendrite microstructures of Pb and S, and Cu segregating around the arm of dendrite. Ag was segregated in the matrix and not combined with dendrite. X-ray Diffraction (XRD) also confirmed the existing of PbS and Cu₂S in all samples. AgCuS was found only in Sample 1 and 3. The hardness of lead niello bars was increased with the increasing of Cu and S composition contents. Some metallurgical aspects of modern lead free niello bar [2-3] were also investigated and compared. The composition of 32 wt%Sn-14 wt%Ag -34 wt%Cu-20 wt%S lead free niello bars was mixed and revealed. It mainly contained Cu₂S, Ag, and SnS. The vicker hardness of lead free niello bars, which was 182±19.1 was higher than lead niello bars which is 83.26±7, 96.87±6.8 and 99.84±5.4 for sample 1 (44.66 wt%Pb-33.99 wt%Cu-11.13 wt%Ag-10.31 wt%S), sample 2 (50.53 wt%Pb-29.94 wt%Cu-1.43 wt%Ag-14.35 wt%S) and sample 3 (40.76 wt%Pb-31.13 wt%Cu-8.36 wt%Ag-19.79 wt%S), respectively.

Samples and Methods: (should use past tense)

The experiment was carried out in two steps. The first step is to investigate microstructure and properties of traditional nielloware with lead contents to understand the microstructure and property relations. Then, the second step is to innovate modern nielloware without lead to mimic microstructure of traditional nielloware and compare the properties. Three sources of traditional nielloware with lead contents had been explored from various provinces in Thailand. The chemical compositions of niello bar were mainly characterized by X-ray Florescence (XRF). Scanning Electron Microscopy (SEM) technique was also observed and analyzed chemical compositions using Electron Dispersive Spectroscopy (EDS)of each phase in microstructure by the mapping technique. The X-ray Diffraction(XRD) had been carried out to observe crystallography. Finally, the hardness measurement were defined by a Micro-Vicker Hardness system. On the other hand, the samples of a modern nielloware without lead were innovated at Srinakharinwirot University to find microstructure close to a traditional nielloware. Hardness and microstructure have been compared to their properties. The niello bar both lead and lead free alloys had been tested by goldsmith to observe the flow of metal which heating. It is also observed the finish product looks.

Results

The results of chemical composition of Lead niello bar characterized by XRF are showed in table 1.

Table 1. The chemical composition and hardness of Lead Niello bar from three various sources.

Lead Niello bar	Pb(wt%)	Cu(wt%)	Ag(wt%)	S (wt%)	HV(mean)
Sample 1	44.66	33.99	11.13	10.31	83.26±7
Sample 2	50.53	29.94	1.43	14.35	96.87±6.8
Sample 3	40.76	31.13	8.36	19.79	99.84±5.4

Scanning Electron Microscopy (SEM) technique was displayed the microstructure. The mapping results are shown in Table 2. The results show dendritic microstructure of Pb and S. Cu segregate around the arm of dendrites. Ag is segregated in the matrix and not combined with Pb. The results of crystal structure by XRD had been analyzed showing that all samples contains the mixing of PbS and Cu₂S. Sample 1 and 3 show AgCuS. Fe element is showed only in sample 2.

Table 2. The microstructure of three samples with mapping results.

	SE Image	Pb	Ag	Cu	S
Sample 1					
Sample 2					
Sample 3					

Once, we obtain composition and microstructure of lead niello bar. We had been tried to mix the composition to obtain microstructure close to the traditional one. The composition of 32 wt%Sn-14 wt%Ag -34 wt%Cu-20 wt%S lead free niello bar were revealed. The microstructure is showed in Figure 1.

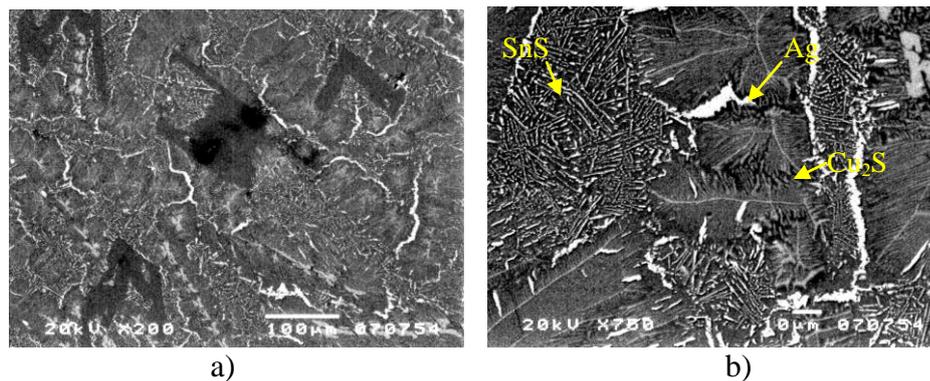


Figure 1. The microstructure of lead free niello bar a) low magnification shows overall microstructure b) higher magnification show dendritic structure

The microstructure of each phase were analyzed by EDS. It shows that it is mainly contained Cu₂S, Ag, and SnS. The hardness measurement was done obtaining the results of 182±19.1. The niello bar both lead and lead free alloys were tested the flowing of niello bar during heating processes making nielloware produced by goldsmith. It shows the same results of nielloware products. However, goldsmith comment that the flowing of lead free alloys during heating which is the process the

niello bar in the groove is stiffer while applying niello bar in the groove. The products are shown in Figure 2.



Figure 2 The niello bar product a) lead niello alloy (the sample were performed on all three composition but shown only one) b) lead free niello

Discussion

Lead traditional niello bars had been investigated from various compositions. Among lead niello bars, sample 3 (40.76 wt%Pb-31.13 wt%Cu-8.36 wt%Ag-19.79 wt%S) which has higher contents of Cu and S shows higher hardness. However, comparing to lead free niello bars, it is softer. As a result of higher hardness, it is more likely that lead free niello bars would give a better polishing surface. The microstructure of lead niello bars revealed dendritic microstructure. The size of dendrite shows small to big dendrite size due to the different chemical compositions and heat treatment history. Nonetheless, all sample are used in commercial giving the same finishing product looks. Therefore, the size of dendrite is not play an important role of properties. Main crystal structures of lead niello bar are PbS and Cu₂S. Lead free niello bars with Sn based alloys are showed that microstructures of lead free niello bars contain dendrite microstructures of SnS, based matrix of Cu₂S and the segregations of Ag which are correlated to the microstructure of lead niello bar. The new alloys of niello bar is tested as a nielloware product obtain the same look of both products.

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