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The Development of Bi-Ag Sandwich Sheets for Fire Assay Applications

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Abstract. A Fire assay is method to verify the fineness of gold with use lead in its process. In this research, Bi-Ag sandwich sheets for a lead-free fire assay method were developed. Bi-Ag sandwich sheets were produced by a hot-dipping method at temperature 300 °C and 400 °C. Samples were characterized the microstructure by SEM along the process. A fire assay method was used to verify and correlate the results of gold fineness to various kinds of wrapping sheets which are Bi-Ag sandwich sheets and lead. The Bi-Ag sandwich sheets shows the layer of 14-20 µm at 300 °C and 8.5-10.5 µm at 400 °C. After cupellation process, the metal beads were observed by SEM and mapping techniques to analyze the remained copper. XRF characterization was confirmed the results of compositions showing an increasing amount of copper as increasing temperature dipping on Bi-Ag sandwich of 0 wt%, 1.58 wt% and 1.34 wt% at S1, S2 and S3, respectively. Higher amounts of copper left on bead buttons consisted with the accuracy of fire assay results which were S1, S2 and S3 obtaining 99.99 wt%, 99.87 wt% and 100 wt% of gold, respectively.

Introduction

Fire assay is a famous and internationally recognized method to verify the fineness of gold with high accuracy, typically within ±0.02% [1]. Therefore the fire assay method has been used widely as a quantitative analytical technique in related industries such as mining and jewelry. The fire assay technique of jewelry industry follows the ISO 11426 method using high temperature at 1050°C -1150 °C to melt lead of 4-6 gram with gold of 200 mg and add metals such as silver at 2.3-3 times of gold weight and copper of 20±5 mg. The process involves the use of lead to collect impurities and separate gold. The noble metals like gold and silver do not react with oxygen or lead oxide, and thus being separated from the melt as a discrete button during the cupellation process [2]. The bead buttons were then rolled and dissolved in nitric acid, termed “parting”, to remove silver. The residue of gold is then weight to calculate and compare to initial gold weight to verify the purity of the gold.

Several researches have been studied using bismuth oxide to replace lead in fire assay processes in mining industry [3, 4]. Recently, there has been an attempt to use bismuth powder to replace lead sheets as an alternative fire assay technique for jewelry applications [5]. It was the first report that successfully determined the gold fineness of commercial gold bars and gold jewelry items with errors only within the range of ±0.05 %.

This research aims to compare results of gold purities by using Bi-Ag sandwich sheets as metal collectors with the results from lead metal collectors of the conventional fire assay technique. Bi-Ag sandwich sheets were processed at two different temperatures of dipping bismuth coating on silver sheets. The microstructure and characterization of bead buttons after cupellation processes were investigated to correlate the results of gold purities with the final results of gold purities.

Materials and Method

Bismuth-Silver Sandwich Sheet Preparation. The metal collectors were prepared by melting bismuth at air atmosphere in a graphite crucible heated with oxygen-gas flame as shown in Fig. 1. The thermocouple was plugged inside the graphite crucible to control the temperature of 300 °C and 400 °C. When the temperature arises to the target temperature with the range of ± 5 ^{o}C, the slags were then removed and rapidly dip the silver sheets. Thickness of bismuth layers were measured by Scanning Electron Microscope (SEM).

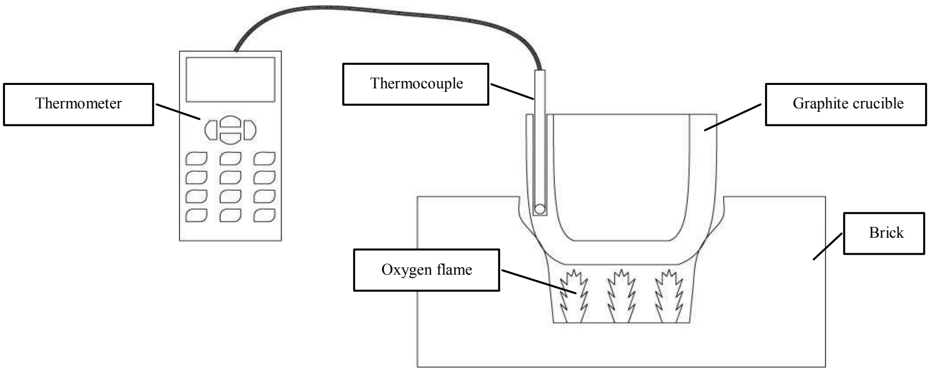

Fig. 1 Schematic of bismuth-silver sandwich sheet preparation

Samples of an Experiment. As in Table 1, the sample No 1 (S1) was used as a standard of fire assay methods according to ISO 11426. The sample No 2 (S2) and No3 (S3) was the 99.9% bismuth of 1 g coating on 99.99% silver sheets of 450 mg at temperature of 300 °C and 400 °C, respectively. All samples uses small grains of 99.99% gold at 200 mg and grains of 99.9% copper at 10 mg. The forms of S1 sample were grains of Ag and Pb sheets and the forms of S2 and S3 used sheet forms. It is note that bismuth powders were added to the samples of S2 and S3 in order to keep the amounts of bismuth to be 1 g while during the fire assay method.

Table 1 Designs of melted button samples

No.	Pb	Bi	Ag	Cu	Au
S1	6 g (sheets)	-	450 mg (grains)	10 mg	200 mg
S2	-	1 g	450 mg	10 mg	200 mg
		(Ag sheets coated with Bi layers)			
S3	-	1 g	450 mg	10 mg	200 mg
		(Ag sheets coated with Bi layers)			

Microstructure and Composition Characterization. After cupellation, the bead buttons were then characterized microstructure on the surface using SEM. The mapping tests on SEM were done to characterize the segregation of elements on bead buttons. The composition data were collected by an X-ray Fluorescence test.

Fire Assay Methods. All samples were placed in magnesia cupels and heated at 1,050 °C for 1 hour to make sure that the alloys were mixed and obtain bead buttons. After that, the samples were rolled to fold and etched with Nitric Acid for two times with the concentration of 33% at the first time and 49% at the second time. Finally, the samples were weight to compare the purity of gold weight before and after the designed process.

Results and Discussions

Bismuth Coat Layers on Silver Sheets. Thickness of bismuth layers were controlled by temperatures of 300 and 400 ^{o}C obtaining the average thickness of 14-20 µm and 8.5-10.5 µm, respectively. The temperature of 300 ^{o}C shows the even coating surfaces on both sides comparing to the uneven interface of 400 ^{o}C displaying in Fig. 2. The intermediate layers of Ag-Bi sandwich sheets at 400 ^{o}C shows more uneven along interface than at 300 ^{o}C indicating instabilities of interfaces due to high temperature of bismuth. It can be explained that the temperature at 400 ^{o}C was too high causing the diffusion layers along the interface. The thin thickness at 400 ^{o}C might be due to higher viscosity losing the surface tensions and low adherence on silver sheets. As a results, the weight of bismuth coating on silver sheets at 400 ^{o}C were then obtained 0.4 g which is less than the process at temperature of 300 ^{o}C obtaining 0.65 g.

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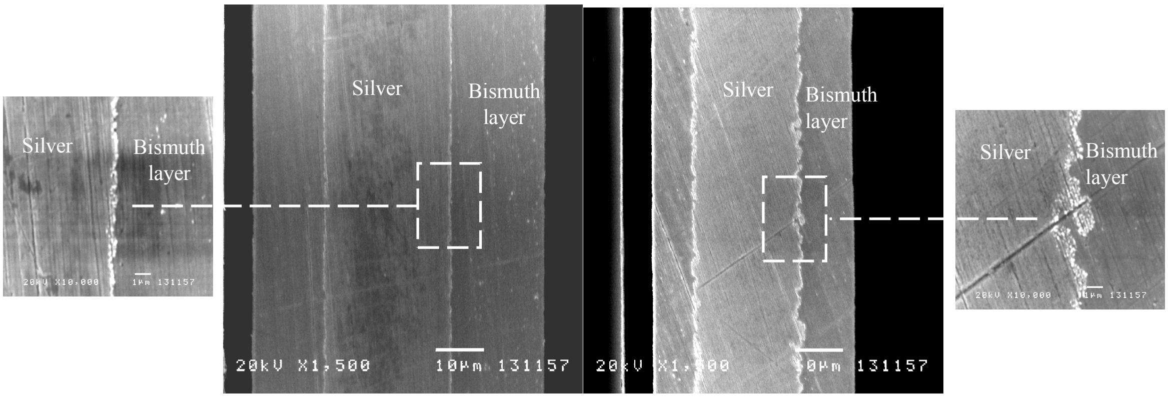

a) b)

Fig. 2 Cross-section of bismuth coating on silver sheets a) 300 ^{o}C and b) 400 ^{o}C

Metal Bead Characterization. After cupellation processes, all metals of each sample were melted to bead buttons. Copper unlike gold and silver was supposed to be absorbed in the cupels by metal collectors such as lead oxides or bismuth oxides. S2 and S3 show that all bismuth oxides revealed amounts of coppers on the surfaces of bead buttons shown in Fig. 3. The analysis of trace elements in metal beads by XRF shows the average of 0.031 wt%, 0.118 wt% and 0.262 wt% of S1, S2 and S3, respectively. The mapping results of S2 and S3 on SEM technique reveal that copper segregates along the edge of the grains but S1 does not occurred the copper along the grains. In Fig. 4, the BSE microstructures of bead buttons show somewhat grain structures at different shape sizes except S3 has no perfect grain structures and irregular shape structures. There were confirmations of Cu segregation along the grain boundaries.

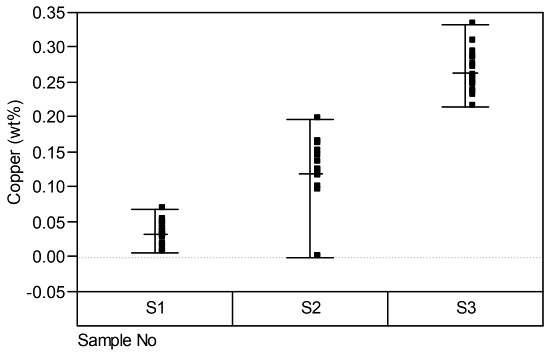

Fig. 3 Impurities of copper after cupellation

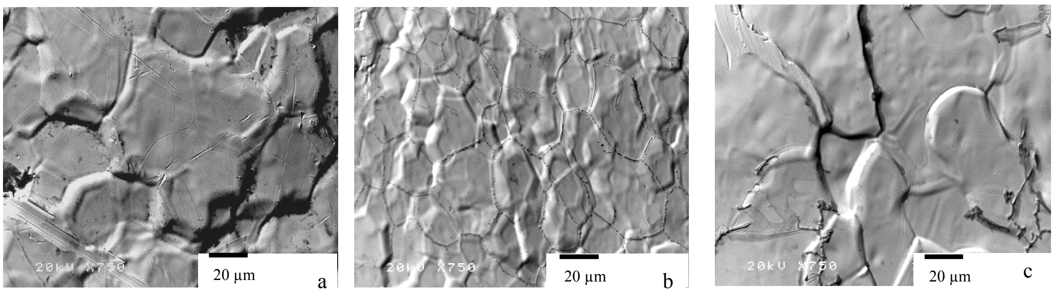

Fig. 4 SEM image at x750 a) Sample No 1 (lead sheets) b) Sample No 2 (Ag-Bi sandwich at 300 ^{o}C dipping) c) Sample No 3 (Ag-Bi sandwich at 400 ^{o}C dipping)

Fire Assay results

The results of fire assay are calculated to confirm purity of gold at 99.99%. The result shows that S1, S2 and S3 obtain the average of 99.99 wt%, 99.866 wt% and 100 wt% of gold, respectively. It can be concluded that Ag-Bi sandwich samples of S2 and S3 has high deviations of 99.99 wt% purity. This is consistent with high amount of copper residues on bead buttons on the surface as shown in Fig. 3.

Conclusion

The Bi-Ag sandwich sheets can be obtained at some certain thicknesses at different temperatures. The cupellation technique with Bi-Ag sandwich sheets has been done obtaining the fire assay results of gold purities. However, the metal collectors of Bi-Ag sandwich sheets reveal the average of gold purity with high standard deviations. This is due to the residues of copper along the grains of lead buttons. To minimize the deviation errors of gold purities, it needs to control the Bi coating on the Ag at the various levels of thicknesses at the controlling temperatures and control the environment of liquids during coating.

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