Application Note AN-PAN-1068

Online analysis of copper, tin, and zinc in white bronze baths by XRF

Galvanic white bronze plating is a decorative and functional electroplating process that deposits a layer of white bronze – an alloy of copper (Cu), tin (Sn), and zinc (Zn) – onto a base metal. White bronze is often used due to its electrical conductivity and resistance to corrosion and wear [1].

Precise chemical analysis techniques are crucial to ensure the quality of the white bronze bath, as they provide valuable insights about the concentrations of various chemicals that influence the plating process. Traditionally, these analyses were conducted in laboratory settings, often utilizing specialized equipment and reagents. However, this approach presents several drawbacks, including extensive turnaround times, substantial financial costs, and the need for dedicated laboratory facilities. These limitations delay the ability to obtain real-time data, which is essential for accurate chemical dosing of the plating bath.

Metrohm offers the 2060 XRF Process Analyzer to address these challenges. This process analyzer uses X-ray fluorescence (XRF) to enable continuous monitoring of chemical concentrations within the plating bath, providing real-time data that guides precise chemical dosing.

INTRODUCTION

Single-metal plating is a viable surface finishing solution. However, there is a limit to how much it can improve a surface's properties. In contrast, co-depositing two or more metals as an alloy coating allows for improvements tailored to specific applications [2].

White bronze is a type of **tri-metal alloy,** meaning it consists of three different metal elements [3]. Specifically, it is an alloy of Cu, Sn, and Zn (otherwise known as CTZ), carefully engineered to provide superior corrosion resistance and a bright, uniform finish.

The white bronze bath used in electroplating considerably improves both the chemical and physical properties of various metal products. When carefully applied to surfaces, the tri-alloy improves corrosion resistance while providing a visually appealing, silvery-white finish [1]. This procedure is commonly used in the manufacture of jewelry and decorative goods, as it increases the durability and appeal of metal products [1].

One of the primary challenges of maintaining a white bronze bath is ensuring the correct ratio of Sn, Cu, and Zn [1]. An imbalance in the concentration of these elements can lead to non-uniform deposits, which affects the aesthetic and functional properties of the plated layer.

Cyanide compounds are often present in white bronze plating baths, primarily because of their ability to form stable complexes with copper [4]. They ensure efficient metal deposition and a smooth, uniform coating. This cyanide-copper complex helps to control the plating rate and improve the overall quality of the finished layer.

Small fluctuations in metal concentrations can significantly impact the performance of the bath. This leads to issues such as dull deposits, fragile coatings, or poor adhesion. These fluctuations can arise from variations in bath replenishment, consumption rates, or contamination. This makes continuous monitoring essential for stable operation.

Traditional monitoring methods often result in process downtime due to the time required for manual sampling, chemical preparation, and analysis. The labor-intensive nature of these methods also increases the potential for human error, which in turns reduces the reliability of the data collected.

Furthermore, the use of cyanide brings significant handling and safety concerns, as it is highly toxic and requires stringent safety protocols to prevent accidental exposure or environmental contamination [5]. Operators must take great care in storing, handling, and disposing of cyanide solutions, which adds an extra layer of complexity to bath

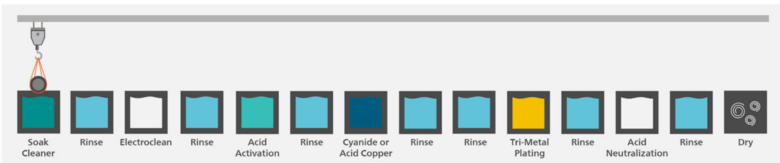

Figure 1. Illustration of a typical copper-tin-zinc (CTZ) alloy plating process flow. Extracted from [1].

APPLICATION

White bronze bath samples were measured using a tungsten anode source XRF spectrometer. This system ensures high accuracy for Sn, Cu, and Zn detection by using characteristic X-ray excitation. Figure 2 shows the generated spectra with distinct peaks corresponding to Sn, Cu, and Zn in the electroplating bath solution.

While the 2060 XRF Process Analyzer (Figure 3) provides real-time monitoring of the metal concentrations in plating solutions, complementary techniques such as titration can also be incorporated to monitor additional critical bath parameters – like pH and cyanide levels. This combination of methodologies not only enhances process control but also provides a comprehensive solution unique in the market, allowing operators to ensure both plating quality and operator safety with a single, integrated analytical approach.

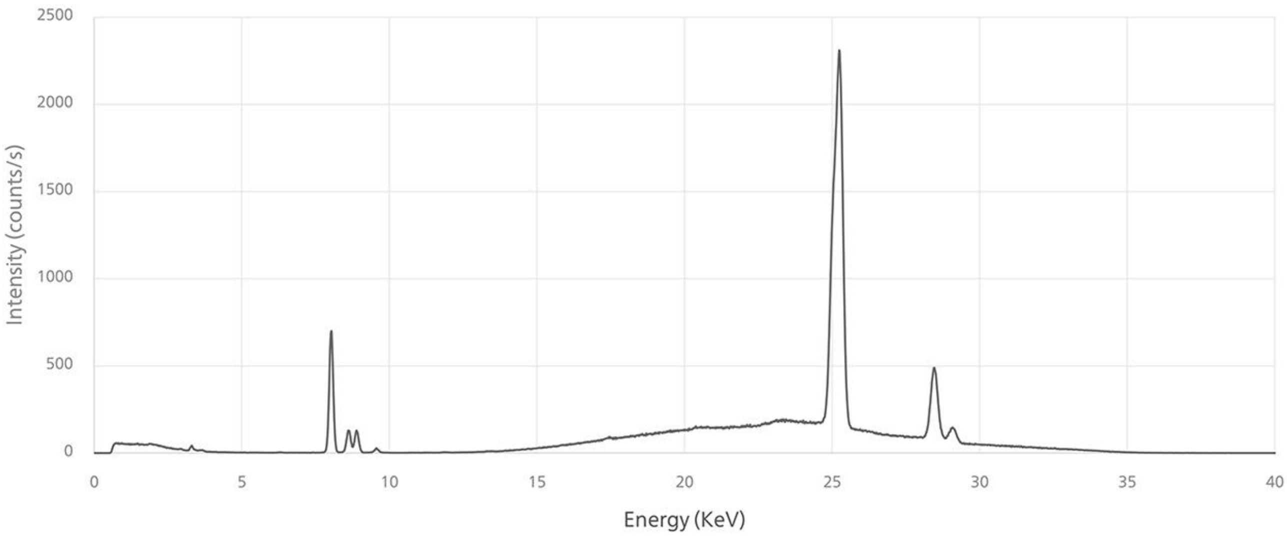

Figure 2. Spectrum generated during XRF measurement of a white bronze plating bath sample. The peaks around 25 and 28 KeV indicate the presence of tin. The peaks around 9 KeV reveal the presence of both copper and zinc, showing their Kα and Kβ lines. The wide, broad peak around 1–4 KeV is likely to be potassium.

Table 1. Measuring range, standard deviation, and relative standard deviation of Sn, Cu, and Zn in white bronze bath samples measured with the 2060 XRF Process Analyzer.

Parameters	Measuring range (g/L)	Standard deviation (g/L)	Relative standard deviation (%)
Tin	21–40	0.351	0.87
Copper	6–15	0.025	0.33
Zinc	0.6–2.5	0.004	0.58

REMARKS

While XRF enables fast and accurate analysis of total metal content, voltammetry (VA) offers the added advantage of distinguishing free Cu2+, Zn2+, and Sn2+ ions, rather than measuring only their total concentrations. Distinguishing between these species is particularly important for monitoring the Sn(II)/Sn(IV) balance which is crucial for bath stability and plating performance. It also ensures that metal ion availability supports optimal deposition rates and bath efficiency.

Figure 3. 2060 XRF Process Analyzer for the analysis of CTZ content in white bronze baths.

CONCLUSION

An XRF electroplating bath analyzer provides a fast and reliable solution for real-time monitoring of Sn, Cu, and Zn concentrations in white bronze plating baths. With its speed, ease of use, and nondestructive nature, it is an ideal tool for optimizing and controlling the plating process. Using X-ray fluorescence for this purpose helps maintain deposit quality and reduces operational costs.

To further improve process efficiency, Metrohm Process Analytics offers the 2060 XRF Process Analyzer which enables automated online monitoring and provides continuous, real-time insights into bath chemistry.

RELATED APPLICATION NOTES

AN-PAN-1064 Monitoring complexing agents in galvanic baths inline with Raman spectroscopy

AN-T-223 Analysis of electroplating baths

AN-T-024 Metal contents of alkaline plating baths for cadmium, copper, lead or zinc

BENEFITS FOR ONLINE PROCESS ANALYSIS

- **Enhanced bath control** – real-time data allows for precise chemical dosing, optimizing bath conditions, and ensuring consistent plating quality.
- **Minimized waste** – accurate chemical dosing reduces the risk of overdosing or underdosing, which minimizes chemical waste and thus environmental impact.
- **Improved process efficiency** – real-time monitoring enables proactive adjustments to bath conditions, which prevents plating defects and process downtime.
- **Reduced labor costs** – the need for frequent laboratory analyses is eliminated, which reduces reliance on laboratory technicians.

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CONFIGURATION

2060 XRF Process Analyzer

Le **2060 XRF Process Analyzer** est un appareil d'analyse de processus en ligne non destructif utilisant une technologie de fluorescence X à dispersion d'énergie (EDXRF). Cet analyseur garantit un contrôle précis et pratiquement en temps réel de flux d’échantillons liquides au sein de processus industriels.

Capable de connecter jusqu'à 20 points d'échantillonnage, le **2060 XRF Process Analyzer** facilite une analyse XRF en ligne transparente. Dans le cadre de la plateforme 2060, il intègre parfaitement plusieurs techniques d'analyse dans une seule plateforme unifiée. Découvrez la puissance de l'association XRF avec le titrage ou la photométrie pour obtenir des informations complètes sur les processus comme jamais auparavant.