



Analytical note

X-ray fluorescence determination of Sn, Sb, Pb in lead-based bearing alloys using a solution technique

Lunfu Tian ^{a,*}, Lili Wang ^a, Wei Gao ^a, Xiaodong Weng ^b, Jianhui Liu ^a, Deshuang Zou ^a, Yichun Dai ^a, Shuke Huang ^a^a Institute of Machinery Manufacturing Technology, China Academy of Engineering Physics, Mianyang 621900, China^b Military Delegate Room of PLA Rocket Force in CAEP, 621900, China

ARTICLE INFO

Article history:

Received 26 April 2017

Received in revised form 25 December 2017

Accepted 21 January 2018

Available online xxxx

Keywords:

Lead

Antimony

Tin

X-ray fluorescence spectrometry

Internal standard

Solution technique

ABSTRACT

For the quantitative analysis of the principal elements in lead-antimony-tin alloys, directly X-ray fluorescence (XRF) method using solid metal disks introduces considerable errors due to the microstructure inhomogeneity. To solve this problem, an aqueous solution XRF method is proposed for determining major amounts of Sb, Sn, Pb in lead-based bearing alloys. The alloy samples were dissolved by a mixture of nitric acid and tartaric acid to eliminate the effects of microstructure of these alloys on the XRF analysis. Rh Compton scattering was used as internal standard for Sb and Sn, and Bi was added as internal standard for Pb, to correct for matrix effects, instrumental and operational variations. High-purity lead, antimony and tin were used to prepare synthetic standards. Using these standards, calibration curves were constructed for the three elements after optimizing the spectrometer parameters. The method has been successfully applied to the analysis of lead-based bearing alloys and is more rapid than classical titration methods normally used. The determination results are consistent with certified values or those obtained by titrations.

© 2018 Published by Elsevier B.V.

1. Introduction

Lead-antimony-tin (Pb-Sb-Sn) alloys, one of lead-based bearing alloys, have been extensively used in aerospace, electronic communications, mechanical manufacture, chemical and nuclear industry due to their high density, low melting point, small friction resistance, excellent plasticity and reasonable electric conductivity [1,2]. The quality of Pb-Sb-Sn alloys is highly dependent on the content of alloying constituents as they have greatly effects on the mechanical and physical properties of these alloys. Therefore, accurate determination of Pb, Sb, Sn in these alloys is very essential.

The content of tin, antimony and lead is relatively high (Sn: 1%–18%, Sb: 6%–18%, Pb:70%–90%), and in most cases, they are determined by conventional titration methods. However, these classic titration methods are too cumbersome and time-consuming in practice to meet the requirement of rapid analysis. Other methods, such as spectrophotometry [3–5], atomic absorption spectrometry (AAS) [6,7], atomic fluorescence spectrometry (AFS) [8,9], inductively coupled plasma-optical emission spectrometry (ICP-OES) [10], inductively coupled plasma-mass spectrometry (ICP-MS) [11], have been implemented for the analysis of trace amounts of Pb, Sb and Sn. However, these techniques are not very suitable for high content element analysis because

extreme sample dilution required by these techniques would bring great errors. To overcome these limitations, there is a demand to develop a rapid and accurate method for the determination of the alloying elements in Pb-Sb-Sn alloys.

XRF is a rapid, multi-element method for the chemical composition study, and has been widely used in the of metallurgy [12,13], geology [14,15], environment [16,17], biology [18,19], food [20], and so on. Thus, this method offer a possibility of simultaneous and quick analysis of Pb-Sb-Sn alloys. Tadeusz Gorewoda [12] and Jose Ward C [21] had used XRF to determine major elements in Sn–Pb solder. This Sn–Pb solder is a tin-based binary alloy, its microstructure and matrix effects are different from Pb-Sb-Sn ternary alloy. Consequently, these reported methods cannot be used for the analysis of Pb-Sb-Sn alloy. For the XRF analysis of Pb-Sb-Sn alloys, the sample preparation technique should be taken into account because the sample preparation has a serious effect on the results. The forms of sample prepared for XRF analysis can be solid metal disk and solution. For solid metal disk technique, direct XRF analysis has the advantage in speed, however, it suffers from significant absorption and enhancement effects of the matrix (lead). In addition, Pb-Sb-Sn alloys have different microstructure [22,23], directly analysis will bring considerable errors due to the composition segregation. For solution technique, it has an advantage in that the analytical results are representative of the bulk sample and not just of the surface, and the effects of microstructure inhomogeneity, non-representative surface composition and surface texture can be eliminated. Hence, it is

* Corresponding author.

E-mail address: gao_wei@caep.cn (L. Tian).

decided to use a solution technique to prepare samples for XRF analysis of Pb-Sb-Sn alloys. For solution technique, matrix effects, instrumental and operational variations will bring un-negligible error. Fortunately, these problem can be settled by internal standard method. In this work, various parameters such as sample dissolving method, sample volume, internal standard, matrix effects, accuracy and precision are investigated in detailed to obtain best analytical results. This method requires less skill and can meet the demand of application.

2. Experimental

2.1. Equipment and reagents

A PANalytical PW4400 wavelength-dispersive X-ray spectrometer, equipped with a rhodium target X-ray tube and a computer with SuperQ 4.0 software, was used for this application. The measurements were performed in the helium with the generator operated at 4 kW. The mask between the sample and the collimator was set to view a 27 mm circular area of each sample. The measurement of standards and samples was carried out in a specially designed PTFE liquid cell with a mylar film window of 6 μm thickness. The analytical lines used for each elements and the measurement conditions were given in Table 1.

All reagents, unless stated otherwise, were of analytical-reagent grade or spectroscopically pure: pure lead, pure antimony, pure tin, bismuth nitrate, nitric acid, tartaric acid.

2.2. Sample preparation

Stock solutions of Sn, Sb and Pb were used for the preparation of calibration solutions, and these stock solutions were made by dissolving high-purity tin, antimony and lead in a mixture of diluted nitric acid (50%) and tartaric acid, respectively. The final concentration of Sn, Sb and Pb was 5.0, 5.0 and 25.0 mg/ml, respectively. A set of calibration solutions were prepared by mixing different volumes of Sn, Sb, and Pb stock solutions to cover the ranges 1–18%Sn/6–18%Sb/balance Pb, total metal weight 0.5 g in a 50 ml volumetric flask, and a 5 ml Bi internal standard solution (10 mg/ml) was added to each solution.

For analysis of Pb-Sb-Sn alloy sample, 0.5000 g alloy chips were dissolved in a mixture of 15 ml diluted nitric acid (50%) and 2 g tartaric acid by heating. After complete dissolution, the solution was transferred into a 50 ml volumetric flask which was added 5 ml of bismuth nitrate beforehand. Aliquots of 10 ml calibration solution or sample solution was transferred into a PTFE liquid cell for XRF analysis using the instrumental conditions given in Table 1.

3. Results and discussion

3.1. Sample dissolution

To realize XRF solution analysis, the solid alloy sample must be converted into solution sample. Pb-Sb-Sn alloys can be dissolved in concentrated sulfuric acid, however, white lead sulfate precipitation occurred in the solution when diluting with water, which led to the failure of the XRF analysis. Hydrochloric acid and nitric acid were tried to use to dissolve sample, it was found that single hydrochloric acid or nitric

acid could not dissolve Pb-Sb-Sn alloys thoroughly, but the mixture of hydrochloric acid and nitric acid could dissolve them thoroughly. For XRF solution analysis, the acid used in sample dissolution is important because the solvent comprises a large portion of the background. Hydrochloric acid has high mass absorption coefficients, and will cause considerable analytical errors due to the high attenuation of the fluorescent radiation by chlorine. This has been reported by some literature [24,25]. In theory, nitric acid is closest to the ideal solution acid due to its small mass absorption coefficients. Unfortunately, nitric acid alone could not dissolve the Pb-Sb-Sn alloys, and metastannic acid precipitation occurred in the solution. It was found that tartaric acid could prevent hydrolysis of Sb and Sn, and that a mixture of 15 ml nitric acid (50%) and 2 g tartaric acid could dissolve 0.5 g sample thoroughly. The sample could also be thoroughly dissolved when increasing the amount of mixed acid and could not be thoroughly dissolved when the amount of the mixed acid was less than 15 ml, however, high acidity was harmful to the safety of the instrument. Thus, 15 ml nitric acid(50%) and 2 g tartaric acid were used for sample dissolution, and for controlling a acidity of 15% nitric acid-4% tartaric acid.

3.2. Sample volume

The depth of solution in the sample cup must be taken into account because there will be a systematic error if the depth does not meet the infinitely thick criteria. The effects of depth, namely sample volume, on the intensities of the three elements were investigated by samples of different volumes. The results are shown in Fig. 1. It can be seen that the intensity of $\text{PbL}\beta$ keeps constant when the sample volume is more than 6 ml, and that the intensity of $\text{SbK}\alpha$ or $\text{SnK}\alpha$ keeps constant when the volume is more than 8 ml. This indicates that the depth of solution achieves the infinite thickness for the three radiations when the sample volume is more than 8 ml. For this proposed solution technique, 10 ml of sample was chosen for XRF analysis to ensure that the depth of solution met the infinite thickness requirements.

3.3. Calibrations

Directly XRF determination of the alloying elements using solid metal disks will introduce considerable errors due to the microstructure inhomogeneity. To solve this problem, an aqueous solution XRF method is proposed for analysis. However, the analysis of solution by XRF is complicated by instrumental variations, evaporation of the liquid and liquid expansion caused by heat effects from the X-ray. For that reason, internal standard method is used to eliminate these adverse factors. For $\text{SbK}\alpha$ and $\text{SnK}\alpha$, Rh Compton scattering ($\text{RhK}\alpha\text{-c}$) was tried as internal standard, and for $\text{PbL}\beta$, $\text{BiL}\beta$ was selected as internal standard because it is next to lead in atomic number and has very similar properties. The intensity of $\text{SbK}\alpha$, $\text{SnK}\alpha$, $\text{RhK}\alpha\text{-c}$, $\text{PbL}\beta$ and $\text{BiL}\beta$ in standard samples were measured, respectively. The respective net intensity or intensity ratio ($\text{SnK}\alpha/\text{RhK}\alpha\text{-c}$, $\text{SbK}\alpha/\text{RhK}\alpha\text{-c}$, $\text{PbL}\beta/\text{BiL}\beta$) were plotted against the corresponding concentrations to form the calibration curves for tin, antimony and lead. As shown in Fig. 2, each calibration curve has better linear relationship using intensity ratio method. The quality of the fit of each curve is checked by residual errors (RMS), which is calculated

Table 1
Measurement parameters used for the analysis.

Line	Crystal	Collimator (μm)	Detector	kV	mA	Angle ($^{\circ}2\theta$)	Peak time (s)
$\text{SbK}\alpha$	LiF220	150	Hiper Scint.	60	50	18.9982	10
$\text{SnK}\alpha$	LiF220	150	Hiper Scint.	60	50	19.8290	10
$\text{RhK}\alpha\text{-c}$	PX10	150	Hiper Scint.	60	50	18.3544	10
$\text{PbL}\beta$	LiF220	150	Hiper Scint.	60	50	40.3318	10
$\text{BiL}\beta$	LiF220	150	Hiper Scint.	60	50	39.0562	10

Download English Version:

<https://daneshyari.com/en/article/7673901>

Download Persian Version:

<https://daneshyari.com/article/7673901>

[Daneshyari.com](https://daneshyari.com)