Quantitative Analysis of Ternary Alloy's Content By means of Laser Induced Plasma Emission Spectroscopy

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Abstract

A quantitative elemental analysis of ternary alloy's content was carried out with laser induced plasma emission spectroscopy. An energetic Nd: glass laser have been focused on a set of alloy targets at reduced pressure. The intensity of UV and visible emission produced from laser-induced plasma was measured using ultra-high sensitive photon detection and counting system of high signal-to-noise ratio. Ternary alloys of Sn-Bi-Pb were used with different composition and the observed photon emission intensity is found to be nonlinearly related to the concentration of the alloy's content. The results were tested and demonstrated that the present sensitive spectrometer can be employed for rapid online estimation of the fractional content of ternary alloys with high accuracy.

التحليل الكمي للسبائك لبثلاثية باستعمال تحليل الطيف للبلازما المنتجة بالليزر

الخلاصة

تم إجراء التحليل الكمي للسبائك الثلاثية باستعمال تحليل الطيف للبلازما المنتجة بالليزر. تم استعمال ليزر نوع نايوديوم – زجاج وقياس شدة الأشعة فوق البنفسجية والأشعة المرئية باستعمال كاشف فوتونات مع عداد. ان السبائك الثلاثة المستعملة هي Sn – Bi – Pb وبتراكيز مختلفة. أظهرت النتائج إن العلاقة بين شدة الفوتونات المنبعثة وتراكيز العناصر هي غير خطية وان الطريقة المستعملة يمكن تطويرها لقياس مكونات السبائك الثلاثية وبدقة عالية.

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Introduction

Materials analysis technology can provide metallurgical and specialist analytical techniques. An extensive range of modern facilities can provide fast, accurate and reliable data. Some of the available techniques include: optical microscopy, neutron diffraction analysis, positron annihilation spectroscopy (PAS), transmission electron microscope (TEM), scanning tunneling microscopy (STM), x-ray scattering, atomic force microscopy (AFM), electron spectroscopy in chemical analysis (ESCA), a combination of electrograph and flow injection analysis, and ion beam for material analysis (IBA). Each of these qualitative and quantitative techniques has a specific region of sensitivity and analytical capability [1-3].

Laser induced plasma spectroscopy (LIPS) with visible, UV and x-ray emission has recently proved to be a powerful laser-based analytical technique due to its simplicity and versatility. It can be employed as an accurate and quick quantitative testing method to measure the composition of materials [4-7]. Moreover, it's a nearly non-destructive method and no special sample preparation is necessary.

The principle of LIPS can be summarized as when a powerful pulsed laser is focused on a surface on an opaque material, a tiny amount of the material is melted, vaporized and through further photon absorption it is heated up until it ionizes. This laser-induced plasma is a micro-source of light that can be analyzed by a spectrometer. Many complicated processes take place in every LIPS experiment, depending on a large number of parameters such as: laser wavelength, pulse duration and power density, spot size, thermal and optical properties of the sample, and pressure of the surrounding gas. For more details see Ref. 8. Theoretical and experimental works [5,9,10] have demonstrated that the target thermal conductivity affects the emission probability, in which the plasma intensity is significantly decreased with increasing thermal conductivity and vise versa.

The present work aims to use LIPS as a tool for ternary alloys quantitative analysis. It depends on the fact that an alloy's thermal conductivity varies uniformly with the type and concentration of their constituent metals, and thereby affecting the emission intensity of plasma. For this purpose, the high sensitivity photon detection system suggested [4] for such application has been used to monitor the changes in emission intensity of plasma produced by the interaction of a pulsed Nd: glass laser with tin-lead-bismuth ternary alloy of different compositions.

Experimental Methods

The LIPS system built and used in this work is shown in Fig. (1). An Nd: glass laser of 1064 nm wavelength and 300 µs pulse duration was used with output
energy in the range of (0.5–5) J. The laser system energy was under close monitoring during each shot using a suitable joule-meter (type ED-200).

A spherical shape vacuum chamber of about 34 cm in diameter was used. A 5 cm dia. glass window was placed in front of the laser pulse as an entrance window. For observation, a quartz window of about 10 cm dia. was placed perpendicular to the laser pulse direction. The target was fixed inside the chamber using a holder equipped with a micrometer for target position adjustment. A focusing lens of 10 cm focal length was mounted inside the vacuum chamber in the laser direction.

The evacuation was achieved using a rotary vacuum pump (type Edwards) and the lowest pressure reached inside the chamber was 0.01 mbar. The intensity of emitted plasma photons is significantly enhanced at low pressures of surrounding gas as previously observed [4] due to the absence of quenching effects.

The plasma emission from UV to visible regions was detected using a fast photomultiplier tube (PMT) manufactured by HAMAMTSU type R212. This PMT works in the range of 185 to 650 nm with a maximum response at 340 nm and short rise time of 2.2 ns. The output signals of PMT were shaped, amplified and counted with a high signal-to-noise counting system (from ORTEC). A single channel analyzer (ORTEC 551) was used to eliminate the noise and discriminate any unwanted signals from real signals related to plasma. The total number of photons detected during a certain adjusted time was monitored using a digital display unit. The accumulation time was fixed at 0.3 s, which covers the whole plasma emission process.

Five different Sn-Bi-Pb ternary alloys were prepared by fixing the lead content at 33%. A hot plate was used with a temperature controller. About 100 g of each Sn-Bi-Pb alloy was prepared by melting a high purity tin in a ceramic crucible. Pure bismuth was added and the temperature was increased until it was melted. After that, pure lead was added and the temperature was increased 25°C above its melting temperature. The molten alloys were poured in a cylindrical stainless steel mold, of 1 cm in height and 3 cm in diameter. Each alloy was then re-melted to insure homogeneity. Ternary Sn-Bi-Pb alloy samples with 10% 20%, 30%, 40% and 50% Sn and fixing lead at 33% were prepared. These targets were polished prior to measurements.

Results and Discussion

Fig. 2 shows the dependence of plasma photons emission intensity on Sn percentage content in the Sn-Bi-Pb alloy. It is obvious that the emission intensity decreases significantly with increasing of Sn concentration in the alloy. This is because that by fixing the lead concentration in the alloy, the change in thermal conductivity (*K*) of the alloy is depending on the thermal conductivity of Sn and Bi in the alloy. As the thermal conductivity of Sn is much higher than that for Bi (note that *K* values are 7.92 and 66.8 W/m.K for Bi and Sn respectively), the thermal conductivity of the alloy thus increases with increasing Sn content in the alloy, and thereby the intensity of plasma emission from the alloy is decreased.

To ensure that this technique is valid and can be applicable in the practical field, a standard ternary alloy that has 33%Sn, 34%Pb and 33%Bi was examined at laser power density of 7.92 × 10^6 W/cm^2 and surrounding pressure of 0.1 mbar. The measured plasma emission intensity for this standard alloy was 49931± 223 counts/shot in comparison with 50050± 224 counts/shot deduced from the best curve fit of Fig. 2. This coincidence in the result (within the experimental error) confirms the high accuracy of the present procedure.

To develop an empirical formula that describes the correlation between the theoretical plasma relative intensity and the experimental one for Sn-Bi-Pb alloy, the plasma emission intensity of pure elements in the alloy, i.e., Sn, Bi and Pb are needed if linear dependence of plasma emission intensity is considered as in equation:

$$I_p = \sum I_i w_i = I_{Sn} w_{sn} + I_{Bi} w_{Bi} + I_{Pb} w_{Pb} \quad \text{….. (1)}$$

where I_p is the plasma emission intensity, $I_{Sn,}$ $I_{Pb,}$ and I_{Bi} is the plasma emission intensity for pure metals, and $w_{Sn,}$ $w_{Bi,}$ and w_{Pb} are the fractional weight of ith

component of the alloy and their summation is equal to unity. Equation (1) can be used to calculate the theoretical plasma emission intensity in for multi-elemental alloys of different concentration of contents.

In general, for an alloy the thermal conductivity can theoretically be approximately be expressed as [5]:

$$K_{alloy} = \sum K_i w_i = K_1 w_2 + K_2 w_2 + K_3 w_3 + \ldots K_n w_n \qquad \ldots\ldots\ldots(2)$$

If one considers linear relationship between the alloy concentration and the thermal conductivity as previously suggested [5,6], then Eq. (2) can be used to deduce the thermal conductivity of any Sn-Bi-Pb alloy. The theoretical and measured results of variation of emission relative intensity with thermal conductivity at 0.1 mbar are plotted in Fig. 3. When using the curve fitting of data in Fig. 3, we got:

$$I_{(R)\exp} = 1 + 5\times10^{-3} K_{alloy} - 3\times10^{-4} K_{alloy}^2 \qquad \ldots.\ (3)$$

$$I_{(R)th} = 1 - 2\times10^{-2} K_{alloy} + 10^{-4} K_{alloy}^2 \qquad \ldots\ldots(4)$$

where $I_{(R)exp}$ is the measured plasma relative intensity for Sn-Bi-Pb alloy, and $I_{(R)th}$ is the theoretical plasma relative intensity. By comparing the behavior of the calculated and measured plasma relative intensity for Sn-Bi-Pb alloy with its thermal conductivity, $I_{(R)th}$, and $I_{(R)exp}$, we can deduce that the assumption of linear dependence can't provide us an accurate results in practice. Accordingly, we suggest that:

$$I_{(R)\exp} = I_{(R)th} \pm \Delta \qquad \ldots\ldots(5)$$

where is a fractional term results due to the affinity of K_{alloy} value to one type of elements in the alloy.

Its value is a function of the alloy's elemental composition.

Conclusions

1- The observed plasma photon emission intensity is nonlinearly related to the concentration of the alloy's content.

2- The present high sensitive spectrometer can be employed for rapid online estimation of the fractional content of ternary alloys with high accuracy. This can be achieved by comparing the relative intensity of the ternary alloy of unknown content with one of its pure components (as a reference).

3- For a direct quantitative determination of content of alloys other than those investigated in the present work, calibration curves (of relative emission intensity versus concentration) are then required.

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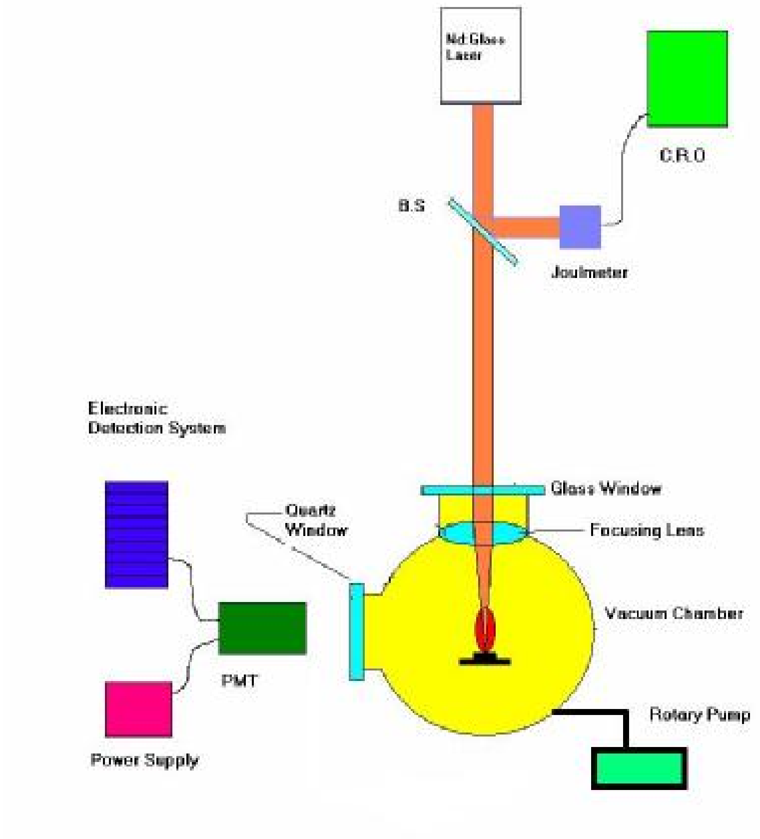

Figure (1) The experimental set-up:

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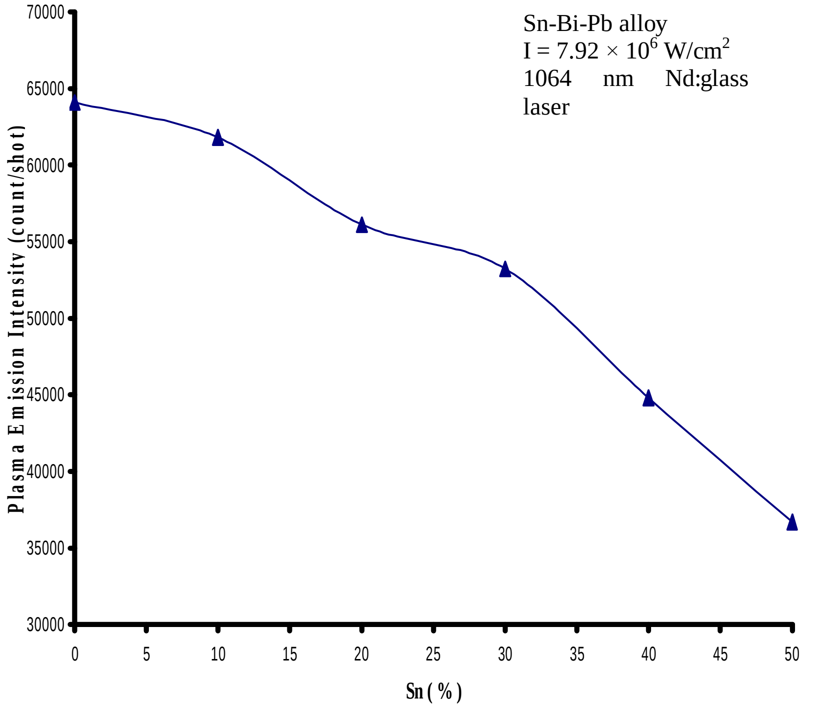

Figure (2) Variation of plasma emission intensity of Sn-Bi-Pb alloy with Sn (%) at 0.1 mbar.

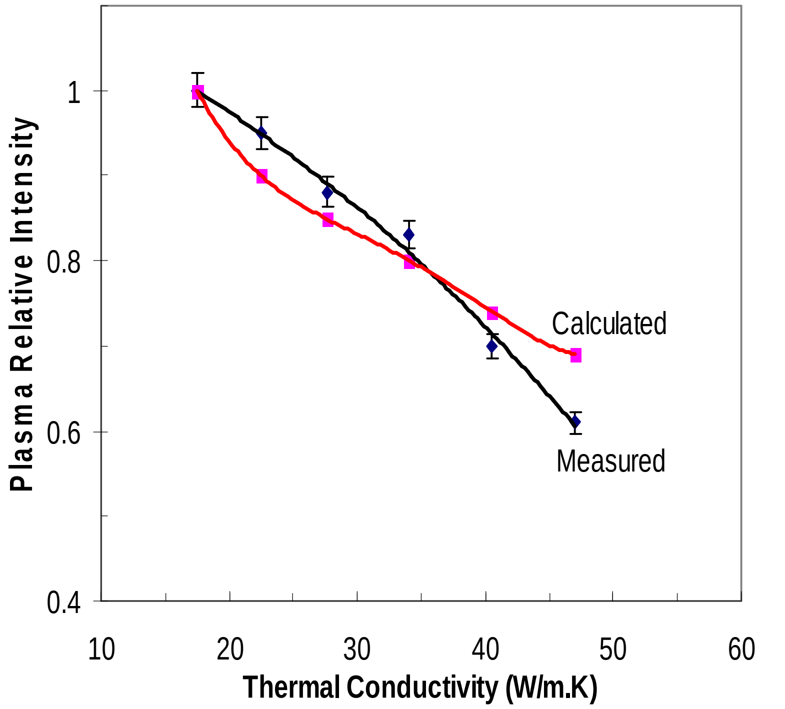

Figure (3) Variation of theoretical and experimental plasma relative intensity with Sn-Bi-Pb alloy thermal conductivity at 0.1mbar