A New Method for Quantitative Analysis of Alloys Content Based on Laser Induced Plasma Emission

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Abstract: In this work, an ultra-high sensitive nuclear detection and counting technique has been used for accurate and quick testing of materials, particularly for determining the concentration of the constituents in a certain alloy. The present method includes the measurement of the intensity of electromagnetic emission from the plasma produced as a result of interaction of laser with the material under test. A small change in the material composition causes a considerable change in its thermal conductivity and hence in the emission intensity. The latter parameter can then be measured with high precision. Measurements were performed with 3 joules Nd: glass laser system and a suitable vacuum chamber. Sets of materials including two different alloy systems (with variable content of constituents) were used. The results demonstrate the capability of the present technique as a new tool for materials testing with performance better than other quantitatively testing techniques since it can be characterized as a non-destructive one and features high accuracy, minimal sample preparation, and rapid analytical capability.

Introduction

Various modern techniques to test and analyse an alloy content are now available, such as the flame atomic absorption technique, x-ray diffraction, neutron activation analysis, transmission electron microscope, electron spectroscopy in chemical analysis, a combination of electrophoresis and flow injection analysis and electrical resistivity. Each of these qualitative and quantitative techniques is based on a specific physical or chemical phenomena and has certain advantages and limitations.

Recently, an additional method to determine the percentage content of an alloy has been developed [1]. It depends on the backscattering of positrons (emitted from a radioactive source) from that alloy in which it depends on its effective atomic number. This method is non-destructive and fast but its sensitivity decreases when the alloy’s constituent metals have close values of atomic numbers. Very recently, the positron lifetime technique has been used [2] as a new non-destructive tool for estimating the concentration of constituent metals in binary alloy systems. This nuclear technique is recommended despite its complicated set-up and data analysis procedure.

Spectroscopic studies of the visible, UV and x-rays emission from the laser induced plasma spectroscopy (LIPS) are a diagnostic tool which have, since the early seventies, been applied to an evaluation of some plasma parameters. However, since the last years, LIPS has been used [3-6] for trace element measurements in some liquids and solids.

The principle of LIPS can be summarized as follows: When a powerful pulsed laser is focused on a certain opaque material surface, its temperature increases rapidly and a tiny amount of the material is vaporized, and through further photon absorption it is heated up until it ionizes. This laser-induced plasma is a micro-source of light since a number of complicated radiative
processes might occur in that plasma. These processes are affected by several parameters such as: laser wavelength, pulse duration and intensity, spot size, thermal and optical properties of the sample surface, and type and pressure of the ambient gas [7,8].

Theoretical and experimental works [9–12] have demonstrated that the target thermal conductivity affects the emission probability, in which the plasma intensity is significantly decreased with increasing thermal conductivity and vice versa. This phenomena valid with moderate laser pulse duration.

In this work, a high-sensitivity photon detection system [12] has been used to monitor the changes in emission intensity of plasma produced by the interaction of a pulsed Nd: glass laser with two different alloys, each contains different metal contents. The present idea depends on the expectation that an alloy’s thermal conductivity may vary with the type and concentration of their constituent metals, affecting the emission intensity of plasma. LIPS can then be employed an accurate and quick quantitative testing method to measure the composition of alloys.

**Experimental Details**

A schematic diagram of the LIPS apparatus is shown in Fig. 1. It consists of the laser system, the vacuum chamber, a plasma emission detector, and the electronic detection system.

The laser system was designed and constructed [13] to produce few joules laser pulses in NIR region. It consists of a pulsed Nd:glass laser of 1.06 μm wavelength and 300 μs pulse duration. The laser rod was pumped with a helical xenon flash lamp supplied from high voltage D.C. power supply. The pulse output energy was varied in the 0.5-3.0 J range and was under close monitoring during each shot using a suitable joule-meter. During the present measurements, the laser power density was $7.2 \times 10^{10}$ W/m$^2$.

A spherical 50 cm diameter chamber with two windows was used. A 10 cm diameter quartz window was mounted at the right angle with the laser beam for observation. The samples were positioned vertically to the incident laser beam on a micrometer-controlled holder and moved during measurements. A focusing lens of 6 cm focal length was mounted in front of the sample, inside the chamber. The chamber was evacuated to 0.1 mbar ultimate pressure to improve the emission intensity. An R212 photomultiplier tube (PMT) was used for fast detection of visible and UV photons emitted from the plasma. The detector response ranges between 185-650 nm with maximum responsivity at 340 nm. Its rise time is 2.2 ns.

**Fig. 1: The experimental set-up:**
1. Nd:glass laser
2. Laser beam
3. Beam splitter
4. Joule-meter
5. Oscilloscope
6. Entrance window (glass)
7. Vacuum chamber
8. Focusing lens
9. Target
10. Plasma plumb
11. Observation window (quartz)
12. Rotary pump
13. PMT
14. PMT power supply
15. Electronic detection system

The output signals from the PMT were shaped, amplified and counted using a high-sensitivity photon detection system. This system consists of a high stability H.V. power supply which is necessary to derive the PMT, and a preamplifier to provide impedance matching between the PMT output and the rest of the electronic system. An amplifier was used to amplify the preamplifier output several hundred times before feeding them to a single channel analyzer (SCA), which is used to eliminate the noise and any other unwanted pulses from the real signals related to the plasma emission. This analyzer produces logic pulses, their number is recorded and displayed by a counter unit. The total number of photons emitted from the plasma
plum per each laser shot can then be determined considering the plum-detector geometry and the quantum efficiency of the PMT.

Two different kinds of binary alloys were used: CuZn and CuAg. Both alloy samples were prepared by mixing the pure elements powder together with different weight percentages (0, 20, 40, 60, 80 and 100%) and then melted each at suitable temperature. The manufactured disks of about 2 mm thick and 3 cm diameter were carefully polished prior to measurements.

The integral intensity of plasma emission in the wavelength range 185-650 nm was measured as a mean of three readings taken at different spots on each investigated sample. The measured intensity varied according to sample constitution between 2000 to 25000 counts per laser shot, and therefore, the statistical error in the whole intensity measurements ranges between 0.5% and 2%.

Results and Discussion

The behavior of relative plasma emission intensity with silver concentration in CuAg alloy is illustrated in Fig. 2. The emission is rapidly decreased with the increase of silver in the alloy, and a clear dependence of emission intensity on the alloy content can easily be noticed. A similar behavior was observed in the case of copper content in CuZn alloy (Fig. 3).

Fig. 2: Dependence of plasma relative intensity on the CuAg alloy content.

Since the thermal conductivity ($\kappa$) of Ag is higher than that of Cu (427 and 398 W/m.K respectively [14]), its value for the CuAg alloy may be increased with the increase of Ag content. Same expectation is hold for CuZn alloy such that its thermal conductivity increases with increasing Cu content (note that $\kappa = 116$ W/m.K for Zn [14]). If one considers a linear dependence of alloy’s thermal conductivity $\kappa_{\text{alloy}}$ on that of the alloy constituents, then,

$$\kappa_{\text{alloy}} = \sum_i \kappa_i w_i = \kappa_1 w_1 + \kappa_2 w_2$$

for binary alloys (1)

where $w_i$ represents the weight (percentage) of the $i$th constitution, and $\sum_i w_i = 1$.

In order to derive empirical equations for the thermal conductivity of CuAg alloy as a function of Ag content, and that for CuZn alloy with Cu content, the best fit of curves given in Figs. 2 and 3 is initially found such that detected plasma relative intensity ($I$) is given by:

$$I = 1 - 0.012 w_{\text{Ag}} + 4 \times 10^{-5} w_{\text{Ag}}^2$$

for CuAg alloy, and

$$I = 1 - 0.014 w_{\text{Cu}} + 6 \times 10^{-5} w_{\text{Cu}}^2$$

for CuZn alloy.

Taking the initial conditions, $\kappa_{\text{CuAg}} = \kappa_{\text{Cu}} = 398$ at $w_{\text{Ag}} = 0$ % and $\kappa_{\text{CuAg}} = \kappa_{\text{Ag}} = 427$ at $w_{\text{Ag}} = 100$ %, one can find:

$$\kappa_{\text{CuAg}} (W/m.K) = 398 + 0.43 w_{\text{Ag}} - 0.0014 w_{\text{Ag}}^2$$

(4)
In similar way, taking $\kappa_{CuZn} = \kappa_{Zn} = 116$ at $w_{Cu} = 0 \%$ and $\kappa_{CuAg} = \kappa_{Ag} = 398$ at $w_{Cu} = 100 \%$, one can find:

$$\kappa_{CuZn} (W/mK) = 116 + 5.13 w_{Cu} - 0.0023 w_{Cu}^2$$

(5)

The extracted dependence of thermal conductivity of CuAg and CuZn alloys on their constituent is illustrated in solid lines in Figs 4 and 5. The linear dependence obtained using Eq.1 is illustrated with dashed lines.

The present results demonstrate the non-linear dependence of thermal conductivity of an alloy with the concentration of its content. One can therefore, generalize Eqs. 4 and 5 for any binary alloy system as:

$$\kappa_{AB\text{ alloy}} = \kappa_A + a w_B + b w_B^2$$

(6)

where $w_B$ is the percentage weight of metal B in the alloy, $a$ and $b$ are constants depend on the alloy constitution and experimental conditions.

As a conclusion, LIPS can be used as a quantitative method to analyze the composition of alloys. It is characterized as a "mostly" non-destructive one and features high accuracy, rapid analytical capability, and practically any kind of samples can be analyzed with no or only minor preparation. This could be the preferred tool for various fields, particularly, in the metallurgy researches and industry sectors.

Fig. 5: Variation of thermal conductivity with CuZn alloy content.

Fig. 4: Variation of thermal conductivity with CuAg alloy content.

The present method can therefore be employed to estimate an alloy's content within few minutes. This can be achieved by comparing the relative intensity of the alloy of unknown content with one of its pure components (as a reference), in the same manner illustrated in Figs. 2 and 3. For a direct quantitative determination of content of alloys other than those investigated in the present work, calibration curves (relative intensity versus concentration) are required.

References

وسيلة جديدة للتحليل الكمي لمكونات السبانك تعتمد على انبعاث البلازما المنتجة بالليزر

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في هذا البحث، تم توظيف تقنية الكشف والعد الفوتوتي بهدف أجراء فحصات دقيقة وسريعة لتركيب المواد وبخاصة تلك المتعلقة بتعيين تركيز مكونات السبانك. تتضمن الطرق المقترحة قياس شدة انبعاث الأشعة الكهرومغناطيسية من البلازما الناتجة من تفاعل ليزر نبضي مع المادة المطلوبةخفضها وأختبار مكوناتها، حيث تتسبب أية تغيرات طفيفة في مكونات مادة ما إلى تغيرات محسوسة في توصيلاتها الحرارية وبالتالي في شدة انبعاث بلازما الليزر والتي يمكن قياسها بدقة متناهية. تم القياسات باستخدام منظومة ليزر النديموم - زجاج النبضي مع حجرة فراغ مناسبة ضمت خصائصاً لهذا المشروع، وأظهرت النتائج نجاح التقنية المقترحة كوسيلة دقيقة وسريعة لأختبار وفحص المواد، تفوق مزاياها طرق الفحص الحالية.