Semi-quantitative analysis of the Neodymium binary alloys using Laser induced breakdown spectroscopy

Seung Hyun Kim[a)], June Sik Ju [a)], Yun Hee Lee [b)], Jeong Hwan Jeong [a)], Hee Sung Sin [a)]
[a)] *Korea Atomic Energy Research Institute, 1045 Daedeokdaero, Yuseoung, Daejeon, Korea*
[b)] *Chungnam National University, 79 Deahakro, Yuseoung, Daejeon, Korea*
kimsh76@kaeri.re.kr

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a laser-based technique that can provide a qualitative and quantitative measurement of a sample in various environments. A measurement was carried out by way of a spectroscopic analysis on plasma directly produced from a high powered Laser ablation on a sample. Its attractive features, such as: minimal sample preparation; fast analysis speed; and operational simplicity; as well as its inherent capability of analyzing all kinds of materials regardless of their physical form and aggregate state, open up wide opportunities for using this technique in the industry, environmental and biological sciences. In view of a Safeguards implementation, the LIBS method has an advantage of a timely analysis of multi elements in a sample taken from a nuclear fuel cycle process when compared to a time consuming chemical analysis method. But, the accuracy of the LIBS is expected to be not favorable due to a high fluctuation in the plasma sphere derived from a Laser. This study is focused on stabilizing a plasma sphere in order to enhance the accuracy of the LIBS.

2. Experimental and Results

This study was to derive an optimized measurement condition with a high reproducibility and to grow a plasma sphere to 20 mm high under a 490±10 mtorr vacuum.

The signal intensity measurement was at a 6.0 mm distance in the direction of a plasma sphere from a sample. This point belongs to the outer sphere region in a plasma. A preliminary experiment was implemented quantitatively on non-radiation elements such as Nd (U replaced element) of the Lanthanide family in a clean lab area, and then the concerned elements, the Uranium.

2.1 Instrumentation of Experiment

Fig.1 shows the LIBS system that was used for the experiment in the Lab. The wavelength of the laser was 1064 nm with a Q-switched Nd:YAG laser, having an output full power of 37.5 mJ, 6 ~ 8 ns of a pulse duration, 2% of an energy stability and 2.8mm of a beam diameter. Spectrometer used a CCD type detector with 14,336 pixels with a 0.1 nm (FWHM) resolution and a 2.1 ms integration time. The gas chamber was manufactured with SUS material having 3 build-in directional quartz windows, and the light emitted from the plasma was collected at a 90° angle by an optical fiber terminated by a lens. The opposite side of the laser input window was located by a sample supporter. A substance motor was installed to minimize a sample surface damage by a high powered laser beam.

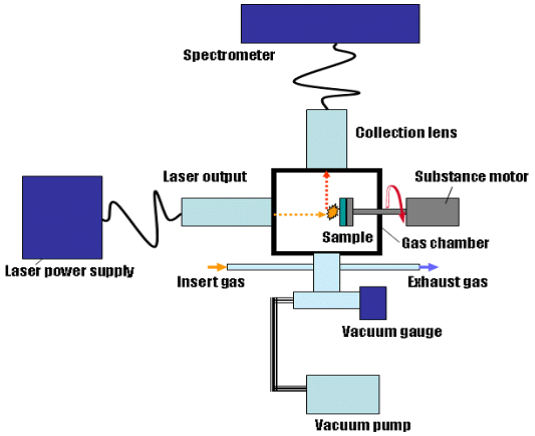

Fig. 1 The composition of actuality LIBS

2.2 Sample Preparation

A preliminary measurement was carried out on the Neodymium prior to a measurement of the Uranium. Four ingot samples which had mutually different components were prepared in a Arc Melting Furnace at 3000℃ starting with a homogeneously mixed powder form of Nd and Cu. Here, Cu is the reference element for each mixed-sample. All of the samples prepared have a thickness of 4.61 mm for the same measurement condition.

Table.1 The description of mixed-samples

Mixed-Sample	Mixture Ratio (weight) Cu : Nd	Atomic Percent		Sample Thickness
		Cu	Nd	
MS-01	2.0 : 0.6	88.24	11.76	4.61 mm
MS-02	2.0 : 1.2	79.15	20.85	4.61 mm
MS-03	2.0 : 1.8	71.59	28.41	4.61 mm
MS-04	2.0 : 2.4	65.49	34.51	4.60 mm

2.3 Derivation of optimized measurement condition

To obtain a signal with a high reproducibility a substance motor was introduced to make a sample revalue for less damage to a sample surface by a high procured laser beam. The optimized measurement condition was found to be at an output power of 18.75 mJ with a gradual increase of the laser power at which the reproducibility was the highest. The plasma sphere

size was sustained at 490±10 mtorr of a vacuum condition for a plasma sphere stabilization.

2.4 Determination of Standard Signals

The measurement was made in the range of 400 ~ 600 nm signals for the Nd and Cu mixed-sample. The signals were taken selectively based on a non-overlapping and the highest reproducibility. The measurements of the standard signals were determined as 430.4 nm for Nd and 510.6 nm for Cu respectively.

2.5 Measurement & Analysis

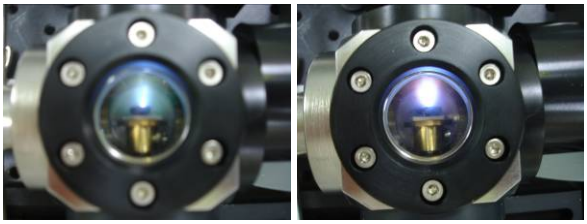

Fig.1 The plasma sphere of mixed-sample 1(left) & 3(light)

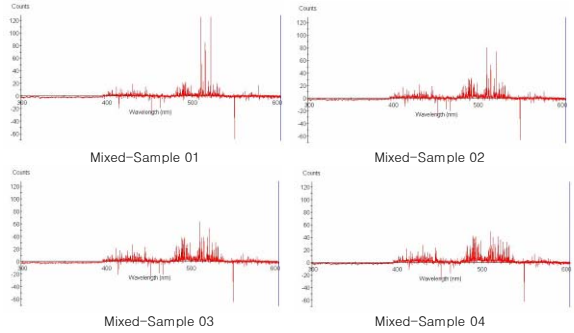

Fig.2 The raw data of LIBS spectrum

Each measurement was performed after 50 laser ablations under the same conditions, and repeated 10 times. The health valuation of the equipments was carried out through a calculated relativity ratio (= signal ratio / atomic ratio). The statistical data of the measurement is shown in Table.2. Here, the result of the measurement was satisfied with a normal distribution, since the p-value was 0.05 or more.

Table.2 The health valuation of LIBS

Relativity Ratio	Means	SD	Kurtosis	Shapiro-Wilk	
				W	p-value
MS-01	1.1947	0.0918	0.2069	0.9067	0.2473
MS-02	1.1434	0.0634	-0.4932	0.8717	0.0999
MS-03	1.0583	0.0282	-0.5546	0.9082	0.2572
MS-04	1.0841	0.0220	2.4367	0.9041	0.2318

The analysis of the measurement was calculated by a simple proportional expression, and the reference sample was chosen as mixed-sample 1. The results are shown in Table.3, and the linear regression of this results was R^2=0.988 (see Fig.3).

Table.3 The result of analysis

	The real Atomic ratio of " Nd"	*LIBS measurement*	*Measurement Error*
MS-02	20.85%	19.98%	- 0.04%
MS-03	28.41%	25.19%	- 11.33%
MS-04	34.51%	31.35%	- 9.16%

※The Reference sample: the mixed-sample 01

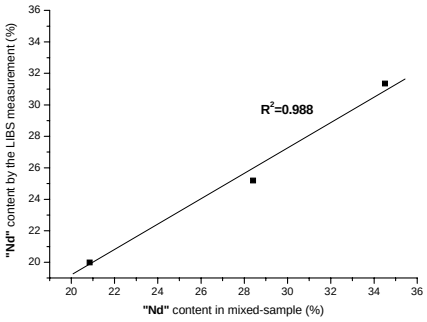

Fig.3 The linear regression analysis of result

3. Conclusions

LIBS is making it possible for a real time measurement on a sample, which displays about 1~6% of a reproducibility and a high normality by a proper adjustment of the laser output, plasma environment, and sample geometry. LIBS measurement values gave an average of a 6.84% measurement error from that of the real value (the component ratio when we manufactured mixed-sample) through a measurement location adjustment of the derived plasma. Further effort is needed for an enhancement of the measurement reproducibility by means of a quantitative analysis of a varied mixture of the Lanthanide family elements (Nd, Sm) and a varied concentration of the Uranium sample.

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