

Journal of the Korean Physical Society, Vol. 61, No. 1, July 2012, pp. 49~54

A Comprehensive Study of H Emission in a TEA CO₂ Laser-induced Helium Gas Plasma for Highly Sensitive Analysis of Hydrogen in Metal Samples

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(Received 4 October 2011, in final form 30 April 2012)

Our previous work on an innovative method of hydrogen (H) analysis using the specific characteristics of a TEA CO₂ laser, “selective detection method of H”, has been improved to realize a high H sensitive analysis with a detection limit of several $\mu\text{g/g}$. For this purpose, first, we clarified the origin of the H emission disturbance coming from H₂O molecules; namely, we showed that most of the H emission came from H₂O on the metal surface and not from H₂O existing in the surrounding gas when we formed a laser-induced gas plasma. Second, the difference in the emission characteristics between the H emission from H₂O on the metal surface and H emission from inside in sample was studied to determine the optimum gating time of the optical multi-channel analyzer (OMA). Third, the gas plasma was totally covered by fresh helium gas using a big pipe (5 mm in diameter) and by flowing a high amount of He (10 l/min). Also, we demonstrated that our methods could potentially be applied to H analysis in steel samples, where an H analysis with a sensitivity of less than 1 $\mu\text{g/g}$ is required without employing a heating process, by removing H₂O on the sample surface with the aid of defocused TEA CO₂ laser irradiation. Thus, we stress that our method can be used for a highly sensitive, *in-situ* analysis of H for metal samples.

PACS numbers: 52.50.Jm

Keywords: Hydrogen analysis, Excitation through helium metastable, Selective detection of H, LIBS, TEA CO₂ laser, Laser-induced gas plasma, Zircaloy sample, Hydrogen analysis in film

DOI: 10.3938/jkps.61.49

I. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) was recently shown to be a promising technique for rapid quantitative analysis of elements in many kinds of samples,

including metals [1–4]. The most interesting advantages of standard LIBS are the ability to perform *in-situ* analysis and fewer sample pretreatments. However, highly sensitive and reliable analysis of hydrogen in metal samples is very difficult with the standard LIBS technique due to a broadening of the H emission spectrum [5,6], a mismatching effect [7–9], the disturbance from ubiquitous water molecules (H₂O) [9], and interference from

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host lines near the hydrogen emission (656.3 nm) line.

Alternatively, hydrogen analysis is essential for studies related to the application technology in nuclear power stations [9]. In light-water nuclear power stations, a zircaloy tube is used as a vessel for uranium fuel. During operation, hot water reacts with the zircaloy surface to produce H_2 gas, which then penetrates and accumulates in the zircaloy tube, causing unacceptable structural damage and critically reducing the strength of the material. Therefore, hydrogen inspection in zircaloy tubes must be performed periodically in a nuclear power station. Commercial methods for detecting hydrogen in such cases generally employ gas chromatography, requiring the melting of a portion of the zircaloy tube in a carbon furnace. This method is time consuming and is not an *in-situ* analysis.

In our previous work, we reported a novel “selective detection of H” technique using the specific characteristics of a TEA CO_2 laser in order to address the difficulties associated with H analysis in zircaloy using the laser plasma method [10,11]. Focusing a TEA CO_2 laser on a zircaloy sample containing hydrogen (H) and surrounded by helium gas at atmospheric pressure resulted in the production of a strong helium gas plasma. Only H atoms came out of the metal sample because the sample surface was slightly melted due to the heat of the gas plasma. The H atoms then moved into the region of the helium gas plasma to be excited by metastable helium atoms; however, no host emission line from the sample appeared as ablation of the host elements does not occur. This technique has great potential for the highly sensitive analysis of H due to the absence of host emission lines.

However, the disturbance of H emission from H_2O is still a difficult problem. In our previous work using a zircaloy sample with free hydrogen, H emission appeared to some extent at $65 \mu g/g$ levels. To realize practical application of H analysis on a zircaloy sample in nuclear power station, we must suppress the H emission disturbance to a level of less than $10 \mu g/g$. In this research, we clarified the origin of the H emission disturbance coming from H_2O molecules. Namely, the H emission disturbance was due to H_2O molecules in the sample’s surface and not H_2O in the surrounding gas. We also studied the emission characteristics for emission from the surface and for emission from inside the sample. A preliminary experiment to confirm the realization of the laser cleaning method without a heating effect was also carried out.

II. EXPERIMENTAL SETUP

Figure 1 shows the experimental arrangement used in this study. A TEA CO_2 laser (Shibuya SQ-2000; 3J pulse energy, $10.6 \mu m$ wavelength, 200 ns pulse duration, and $30 mm \times 30 mm$ beam cross-section) was used as an irradiation source. During the experiment, the laser en-

ergy was set at 250 mJ by inserting an aperture in front of the focusing lens. The laser beam was focused on the sample’s surface from the front through a ZnSe window by using a combination of two ZnSe lenses, one with a focal length of 50 mm and the other with a focal length of 100 mm. When the laser cleaning was employed to remove H_2O from the metal surface, the lens with a focal length of 50 mm was shifted 15 mm from the focusing condition. The spot size of the laser beam on the zircaloy surface was $0.5 mm \times 0.5 mm$ for tight focus, resulting in a power density of $0.7 GW/cm^2$. The laser was typically operated at 10 Hz; however, the laser was employed in manual single shot mode for some experiments.

The samples to be irradiated were cleaned with ethanol and attached to a sample holder in a metal chamber. The samples used in this experiment were zircaloy that had been doped with various concentrations of hydrogen (0, 11, 50, and $100 \mu g/g$). Prior to the analysis, the chamber with an inner diameter of 115 mm was evacuated using a vacuum pump to a pressure of approximately 2 Pa, was heated to $150^\circ C$, and held at that temperature for 30 minutes to remove the H_2O attached to the chamber wall. During laser bombardment, high-purity He gas (99.99999%) was passed over the surface through a metal pipe with a diameter of 5 mm. The pipe exit was located close to the focusing point of the gas plasma (at a distance of 3 mm). The helium gas flowed into the chamber from the pipe exit. The pressure of the surrounding gas in the chamber was set to 0.11 MPa.

The emission spectrum of the plasma was obtained by using an optical multi channel analyzer (OMA) system (ATAGO Macs-320) consisting of a 0.32 m focal-length spectrograph with a grating of 1200 grooves/mm, a 1024-channel photodiode detector array, and a micro-channel plate image intensifier. The spectral resolution of the OMA system was 0.2 nm, and the spectral width to display was 60 nm. The light emitted from the laser plasma was collected by an optical fiber (27° solid angle) inserted in a quartz tube and placed 3 cm from the focusing point of the TEA CO_2 laser and perpendicular to the path of the laser beam. The other end of the fiber was fed into the OMA system.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In a previous experiment [10,11], we reported a selective detection technique for H analysis in a zircaloy sample. The method has significant potential for sensitive analysis of H in a metal sample as it is not affected by the host emission lines that appear near the H emission line when the typical LIBS technique is used. In order to suppress the interference from H_2O , we intentionally generated a small-sized helium gas plasma, and high-purity helium gas was flowed using a small pipe (diameter of 2 mm), the exit of which was set near the gas plasma.

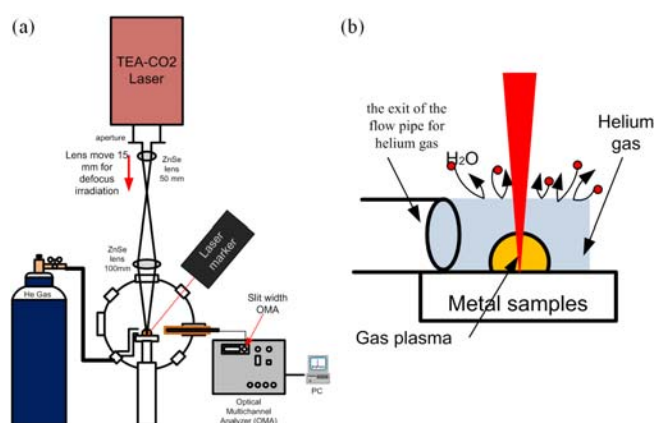


Fig. 1. (Color online) (a) Experimental set-up. (b) Metal-assisted helium gas plasma and helium gas flow system.

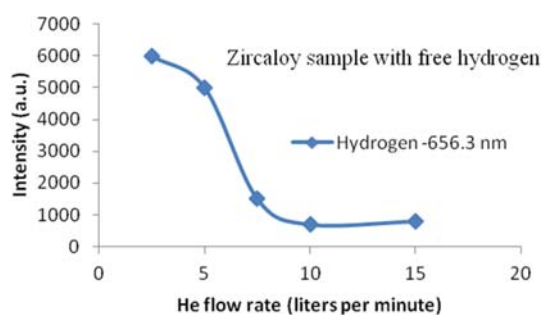


Fig. 2. (Color online) Hydrogen emission intensity (656.3 nm) as a function of the helium flow rate in zircaloy samples containing free hydrogen.

In this study, we modified the helium gas flow system by using a large-diameter pipe (approximately 5 mm) so that the helium gas plasma was totally covered by fresh gas, which protected the helium gas plasma from being attacked by H₂O molecules as there are impurities in the surrounding gas, as shown in Fig. 1(b). If the helium gas plasma is to be fully covered with fresh helium gas, the helium gas must flow at a sufficient rate.

Figure 2 shows how the hydrogen emission intensity (656.3 nm) changes with the helium flow rate. The spectrum was acquired from the zircaloy sample with free hydrogen. Thus, the emitted hydrogen came from H₂O attached to the sample's surface or contained in the surrounding gas. The delay time and the gate width of the OMA system were set at 1 and 10 μ s, respectively. Each data point plotted in the curve was obtained using ten shots of laser irradiation and was acquired using a new position on the sample's surface. The intensity of the H emission at 656.3 nm steeply decreased with increasing He flow rate up to ten liters per minute and then become nearly constant. Based on this experiment, a He gas flow rate of ten liters per minute rate was used in subsequent experiments. This technique enables H emission to be suppressed to approximately 10 μ g/g.

As described above, a host emission line did not appear

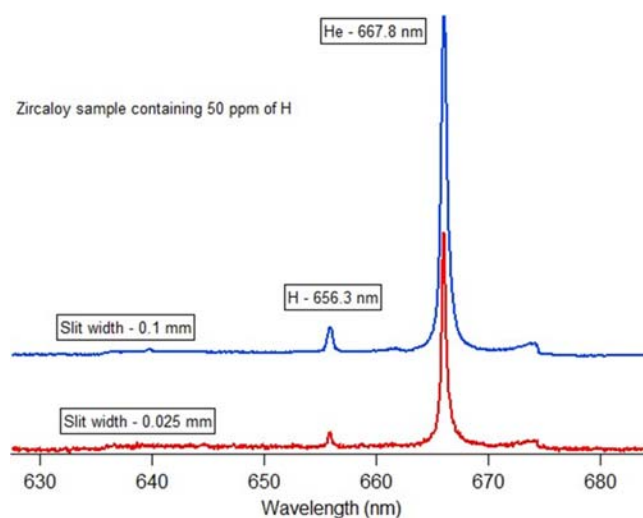


Fig. 3. (Color online) Emission spectra for a zircaloy sample containing 50 μ g/g of hydrogen using a slit width of 0.025 mm (red line) and a slit width of 0.1 mm (blue line).

near the H emission (656.3 nm) for this unique selective detection method, indicating that the slit width of the OMA could be opened further in order to improve the signal-to-noise (S/N) ratio. Figure 3 shows the emission spectra taken from a zircaloy sample containing 50 μ g/g of H with the previously used slit width of 0.025 mm (red line) and with a slit width of 0.1 mm (blue line). The gate condition of the OMA system was set at 1 – 20 μ s, and ten shots of the TEA CO₂ laser irradiation were used. With a slit width of 0.1 mm, the emission intensity was much greater and broader than that with a slit width of 0.025 mm. The S/N ratio using the slit width of 0.1 mm was four times greater than that using a slit width of 0.025 mm. When the slit width of the OMA was greater than 0.1 mm, a disturbance was generated due to the scattering of light in the spectrograph. Based on these results, we used a slit width of 0.1 mm in the subsequent experiments.

If a highly sensitive analysis of H with a detection limit of 1 μ g/g is to be achieved, H emission from H₂O must be reduced further. For this purpose, the origin of H₂O, either from the sample's surface or the surrounding gas, must be understood as it is responsible for the H emission. As a result, emission spectra were collected using the manual single-shot irradiation mode. Figure 4(a) shows the emission spectrum of the first shot of laser irradiation on a free hydrogen zircaloy sample. The H emission (656.3 nm), which comes from H₂O, was relatively strong. Figure 4(b) shows the emission spectrum of the second shot of laser irradiation a few seconds after the first laser irradiation. The laser irradiation was administered at the same position used in Fig. 4(a). The H emission nearly disappeared, indicating that the H emission is primarily due to H₂O molecules that are attached to the sample's surface and that the H₂O in the surrounding gas does not contribute directly to the H emission. If

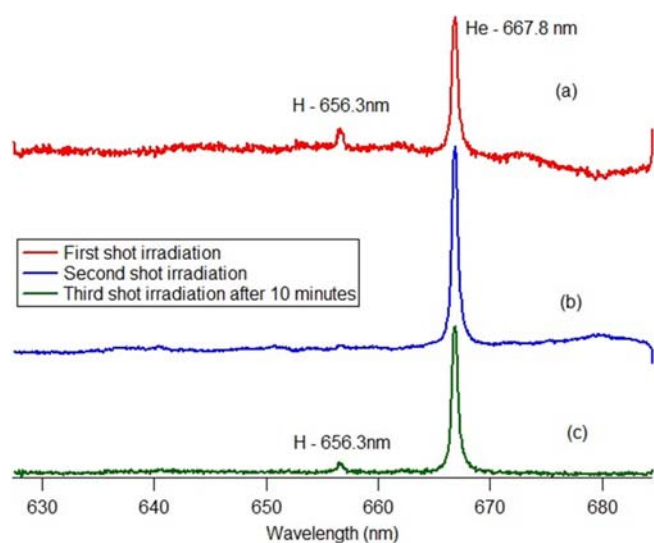


Fig. 4. (Color online) (a) Emission spectrum of a free hydrogen sample after the first single shot of laser irradiation. (b) Emission spectrum after the second single shot of laser irradiation administered a few seconds after the first laser irradiation. (c) Emission spectrum after the third single shot of laser irradiation applied approximately ten minutes after the second laser irradiation.

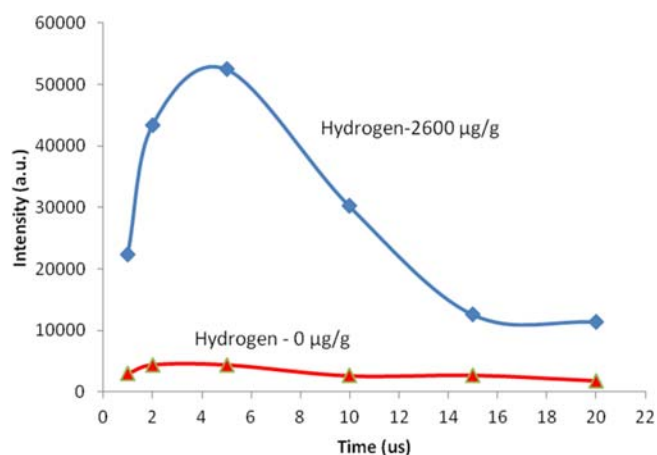


Fig. 5. (Color online) Time profiles of the H-656.3 nm emission from two different samples: zircaloy containing 2600 $\mu\text{g/g}$ of hydrogen (blue line) and zircaloy with free hydrogen (red line).

the origin of the H_2O responsible for H emission were the surrounding gas, H emission would always occur, regardless of previous laser bombardment. Figure 4(c) shows the emission spectrum of the third shot of laser irradiation administered approximately ten minutes after the second shot. H emission was clearly observed, indicating that over the course of ten minutes, a considerable number of H_2O molecules had become attached to the sample's surface.

Another important factor to consider for suppressing H emission from H_2O is optimization of the gating time

of the OMA system because there may be a difference in the emission time profiles between H emission from inside the sample and that from H_2O attached to the sample's surface. Figure 5 shows the time profiles of the H emissions from two different samples: a zircaloy sample containing 2600 $\mu\text{g/g}$ of H (blue line) and a zircaloy sample with free hydrogen (H emission from the surface, red line). The gate width of the OMA system in this experiment was set at 0.5 μs , and the OMA slit width was 0.1 mm. Each data point plotted in the curve was obtained using ten shots of laser irradiation and was acquired using a new position on the sample's surface. In this experiment, we intentionally increased the amount of surface water to produce a sufficient signal corresponding to H emission by not heating the chamber. For the zircaloy sample containing 2600 $\mu\text{g/g}$ of H, H emission increased steeply to 5 μs and then decreased to 20 μs . Because the H emission from the surface continued with a long lifetime, the contribution of H emission from the surface increases when the gate width of the OMA is increased. Therefore, the H emission must be measured at the initial stage of plasma production with the OMA gating time set at 1 – 3 μs .

The long lifetime of H emission from H_2O is explained as follows: Prior to laser irradiation, the sample surface is covered by H_2O molecules. During the initial stage (approximately 0.1 μs) of TEA CO_2 laser pulse irradiation when the helium gas plasma has not yet started to form, the H_2O molecules attached to the sample's surface are dissociated by absorbing the TEA CO_2 laser energy to produce H and O atoms, and the atoms move out at high speed. After approximately 1 μs , the helium gas plasma expands until approximately 20 μs . Because the hydrogen is already distributed in the space in front of the helium gas plasma, metastable helium atoms collide with hydrogen atoms, resulting in H emission. When the plasma completely disappears, the H_2O molecules in the surrounding gas again start to attack the sample surface and become attached.

Based on these experiments, we conclude that the important factors for suppressing H emission from H_2O and increasing the sensitivity of H detection are a high He gas flow rate (ten liters per minute), which can be achieved using a large pipe, a wide slit width of 0.1 mm, pre-surface irradiation, and a suitable OMA gating time setting (1 – 3 μs). A preliminary H analysis experiment was performed under these optimized conditions using zircaloy samples containing different low-level concentrations of H (free hydrogen, 11 $\mu\text{g/g}$, 50 $\mu\text{g/g}$, and 100 $\mu\text{g/g}$). Figure 6 shows the hydrogen emission spectra of zircaloy samples containing (a) 0 $\mu\text{g/g}$ of H, (b) 11 $\mu\text{g/g}$ of H, (c) 50 $\mu\text{g/g}$ of H, and (d) 100 $\mu\text{g/g}$ of H. Each spectrum was obtained after ten shots of laser irradiation at 10 Hz following two shots of pre-irradiation to remove the surface water. The gate time and the gate width of the OMA system were 1 and 2 μs , respectively. Hydrogen emission from the zircaloy containing 11 $\mu\text{g/g}$ of H was observed with a low background emission in-

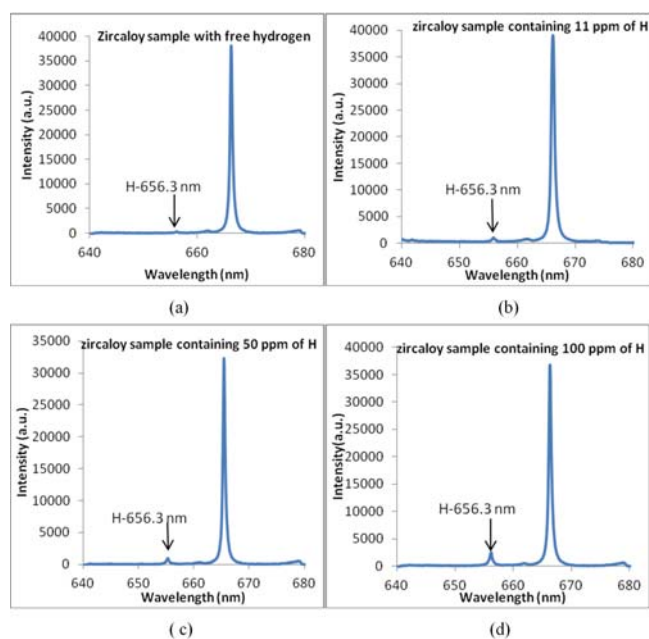


Fig. 6. (Color online) Hydrogen emission spectra of the zircaloy samples containing (a) 0 $\mu\text{g/g}$ of H, (b) 11 $\mu\text{g/g}$ of H, (c) 50 $\mu\text{g/g}$ of H, and (d) 100 $\mu\text{g/g}$ of H.

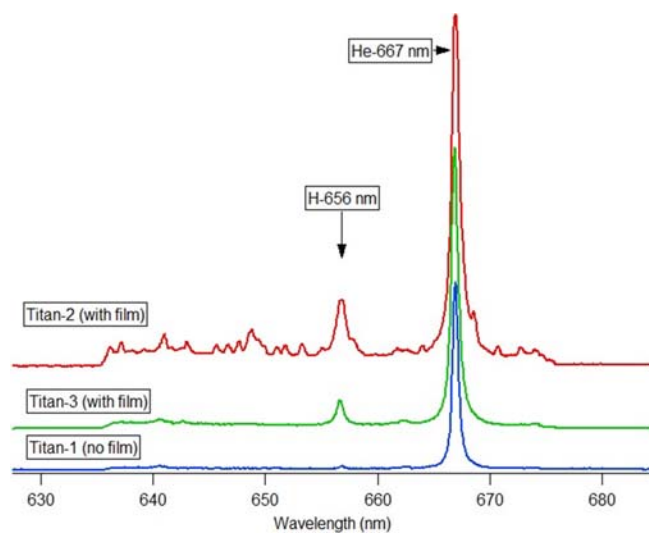


Fig. 7. (Color online) Emission spectra of Titan samples with different films on their surfaces. Titan-2 (red line) and Titan-3 (green line) have coating films on their surfaces. Titan-1 is pure Titan with free hydrogen (blue line) and no film.

tensity, and the H emission from zircaloy 0 $\mu\text{g/g}$ was very small. It should be stressed that a reliable hydrogen analysis can be conducted in a low concentration range between 10 $\mu\text{g/g}$ and 100 $\mu\text{g/g}$ with a detection limit of at least 5 $\mu\text{g/g}$. Experiments with such low concentration levels of H have never been performed before.

With confirmation of our technique's high sensitivity for suppressing the disturbance of H₂O, we fabricated a

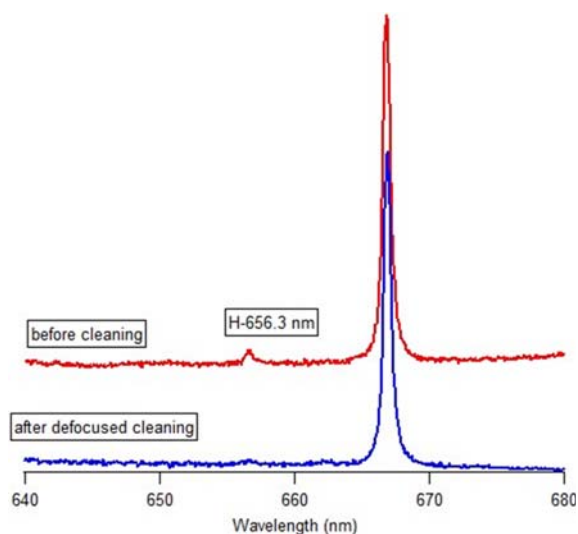


Fig. 8. (Color online) Hydrogen emission spectra of a zircaloy sample with free hydrogen after TEA CO₂ laser bombardment on the surface before cleaning (red line) and after defocused laser cleaning (blue line).

unique H analysis scenario in a Titan thin-film sample. Figure 7 shows the emission spectra of Titan samples with different films on their surfaces (red line and green line) and pure Titan with no film (blue line). The OMA gate condition of the system was set at 1 – 3 μs , the slit width of the OMA was set at 0.1 mm, and the helium gas flow rate was ten liters per minute. In this experiment, we did not use pre-irradiation because it would remove the thin film. The emission spectra of the Titan-2 and the Titan-3 samples are different due to the different surface coating treatment processes. In the spectrum for Titan-1 (blue line) shown in Fig. 7, the hydrogen signal is negligibly weak because there was no thin film on the surface, indicating that H elements in the film can be analyzed. This kind of film analysis is only possible with a TEA CO₂ laser because the induced gas plasma vaporizes only the thin film on the surface, without ablating the sample's body. If we had used a Nd:YAG laser, a strong host line would have appeared due to the ablation process. Additionally, ordinary H analysis using gas chromatograph is not possible because the film and the sample will vaporize, causing loss in the film analysis.

By combining several techniques, we can suppress H emission from H₂O to approximately 5 $\mu\text{g/g}$. The strict requirements of the nuclear power station industry can be satisfied using these techniques. However, the present technique is still not sufficient for H analysis in steel samples, which requires a much greater H sensitivity down to a few $\mu\text{g/g}$. It should be noticed that heating around 150 °C in the chamber and pre-irradiation by using a tight focus condition technique were not permitted when we tried to analyze the hydrogen in steel because the hydrogen from inside was easily removed. To overcome this problem, we used the pre-irradiation technique under a

defocused condition because the TEA CO₂ laser light is highly absorbed by the H₂O molecules in the surface. Figure 8 shows the hydrogen emission spectra from the zircaloy sample with free hydrogen when laser irradiation was made by tight focusing (red line). The gate condition of the OMA system was set to 1 – 3 μ s, the slit width of the OMA was 0.1 mm, and the helium gas flow rate was ten liters per minute. In this experiment, no heat treatment in the vacuum chamber was applied. The remaining H emission, which comes from the surface water, is approximately 50 μ g/g. On the other hand, the blue line spectrum was taken after defocusing cleaning; namely, ten shots of laser irradiation were performed under the defocusing condition, shifting the focusing lens at 15 mm, where almost no gas plasma generation was observed. Then, the lens was immediately set back for a tight focus to produce a helium gas plasma. H emission (blue line) is seen to be very weak (corresponding to approximately 10 μ g/g) compared to that without cleaning (red line). Thus, the defocusing cleaning method was confirmed as being very effective for suppressing H emission from H₂O on the sample's surface. However, our system is not yet sufficient for practical applications because the time interval between the defocus laser cleaning and laser irradiation for plasma generation is approximately two minutes. This time interval is long, which allows many H₂O molecules to attach on the sample's surface. To solve this problem in the future, we will synchronize two TEA CO₂ laser: one for the defocus laser cleaning and the other for the helium gas plasma generation with a suitable time interval (about 100 ms).

IV. CONCLUSION

In this study, we developed a highly-sensitive technique for the analysis of hydrogen in a metal sample, which is typically difficult due to a H₂O disturbance. This novel selective H detection method using a helium gas plasma combined several techniques. First, a gas plasma was produced just near the exit of a large gas pipe, and high-purity helium gas was flowed at a high rate of ten liters per minute so that the helium gas plasma was totally covered by the fresh helium gas. Using a pre-irradiation technique, H₂O on the surface was removed. We confirmed that the origin of the H₂O causing the H emission was the H₂O located on the sample surface and not that in the surrounding gas. The time profiles of hydrogen emission from inside the sample and the sample surface were clearly different. The hydrogen emitted from H₂O on the surface had a long lifetime compared to that emitted from the sample itself. Therefore, in order to suppress the contribution of hydrogen emission from the H₂O, the OMA gate condition was set at 1 – 3 μ s. We demonstrated that a highly-sensitive H analysis was possible for a zircaloy sample containing hydrogen at low concentration levels (11 – 100 μ g/g). The results showed that the sensitivity of the H analysis was more than sufficient to assess hydrogen degradation in

metal materials used in the nuclear industry. We also proved that this technique could be used for H analysis in thin films on Titan samples; in general H analysis in films is usually very difficult because when conventional H analysis using gas chromatography is employed, the film and the sample will be vaporized, which causes loss of information of the H distribution. We confirmed that the defocused cleaning methods were very effective for suppressing the disturbance of the H emission from H₂O on the sample surface. In the future, to achieve H analysis with a precision of 1 μ g/g, we will employ two TEA CO₂ laser systems; one for surface cleaning by defocused laser irradiation and the other for He gas plasma generation.

ACKNOWLEDGMENTS

This work was partially supported by the City Area Program and the Regional Innovation Cluster Program of Ministry of Education, Culture, Sports, Science and Technology (MEXT) in Japan. Part of this work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0026774). This work was also partially supported by a Basic Research Grant in Physics, The Academy of Sciences for the Developing World, Third World Academy of Sciences (TWAS) under contract no. 06-150 RG/PHYS/AS UNESCO FR:3240144882.

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