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H-D Analysis Employing Low-Pressure microjoule Picosecond Laser-Induced Breakdown Spectroscopy

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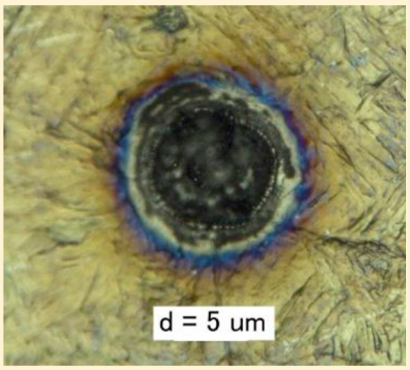
ABSTRACT: An experimental study is conducted in search of the much needed experimental method for practical and minimally destructive analysis of hydrogen (H) and deuterium (D) in a nuclear power plant. For this purpose, a picosecond (ps) Nd:YAG laser is employed and operated with 300−500 μJ output energies in a variety of ambient gases at various gas pressures. The sample chamber used is specially designed small quartz tube with an open end that can be tightly fitted to the sample surface. It is found that ambient Ar gas at reduced pressure of around 0.13 kPa gives the best spectral quality featuring fully resolved H and D emission lines with clearly detectable intensities and practically free from surface water interference. The D emission intensities measured from zircaloy plates containing various concentrations of D impurity are shown to yield a linear calibration line with extrapolated zero intercept, offering its potential application to quantitative analysis. The estimated detection limit of less than 10 ppm is well below the sensitivity limit of around 600 ppm required for the regular inspection of zircaloy tubes in a heavy water nuclear power plant. The use of the exceedingly low laser energy is shown to offer an additional advantage of minimum destructive effect marked by the resulted tiny craters of about 5 μm diameter with 25 μm depth. These results promise the potential development of the desired alternative analytical tool for regular in situ and real time inspection of the zircaloy tubes in a heavy water power plant.



The large and unique advantages offered by nuclear energy are so far unmatched by other alternative new energy sources in meeting the pressing demand for large-scale and high-efficiency energy supplies.[1] Inspite of the rare and isolated nuclear accidents that happened in the past, many new nuclear power plants are being built and on the drawing board for their realization in the near future. These new power plants are generally designed with largely improved safety control and many of them employ the heavy water moderator for economic benefit. Meanwhile, there remains one long-standing problem to be tackled for enhancing the efficiency of the reactor operation. In a nuclear power reactor, the uranium fuel is contained in zircaloy tubes which are immersed in a water tank. During the operation of the reactor, hot water reacts with the zircaloy at its surface to form zirconium oxide and hydrogen or deuterium gas which readily penetrates into and accumulates in

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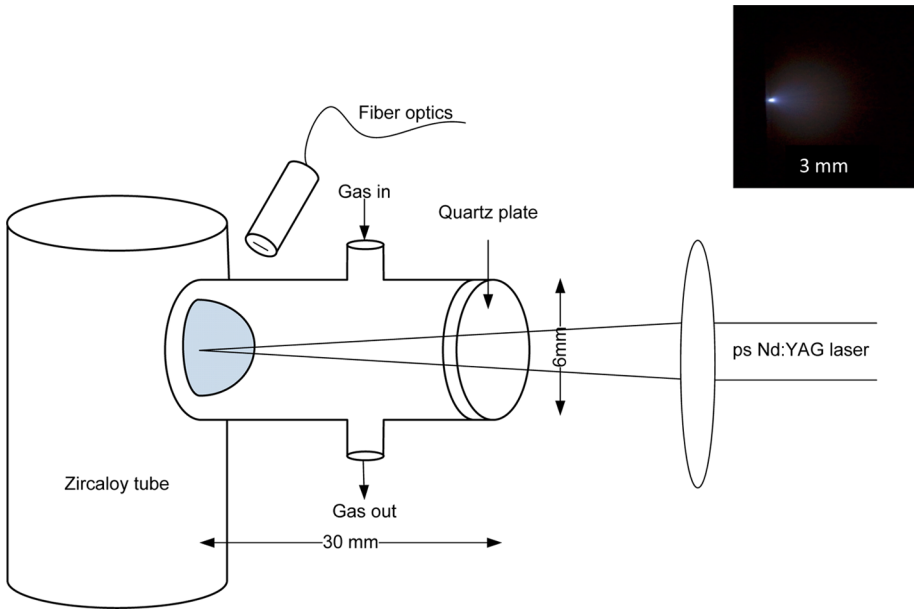

Figure 1. Schematic representation of the experimental setup using specially designed small cylindrical chamber having an open end equipped with flat O-ring that can be tightly fitted to the sample surface.

the zircaloy tube. The excessive presence of these trapped hydrogen or deuterium atoms are known to cause a certain structural damage leading to reduced mechanical strength of the zircaloy tubes and may potentially endanger the operation of the power plant. Therefore, the H and D concentrations in the zircaloy tubes must be examined periodically. A standard technique currently adopted for detecting hydrogen involves the use of a gas detector and requires melting off a portion of the zircaloy tube in a carbon furnace, which is followed by a special handling to removal the remaining fuel in the tube. Thus, it is highly desirable to replace the existing tedious, time-consuming and destructive method by a more practical and minimally destructive one. In particular the demand of improved D detection technique in the heavy water nuclear power plant must be addressed in view of its anticipated rapid growth in the near future.

As reported previously,[2] it is indeed possible to improve the H and D detection method by means of some technical modification of the laser-induced breakdown spectroscopy (LIBS) which has become a widely adopted modern tool for rapid spectrochemical analysis in industries and research laboratories.[3−11] Using atmospheric pressure ambient He gas and double pulse configuration, the detection of sharp H I 656.28 nm and D I 656.10 nm emission lines from the zircaloy sample was successfully demonstrated,[12−14] overcoming the long-standing problems of Stark broadening effect and intensity diminution due to the time mismatch effect commonly encountered in the standard operation of LIBS conducted with atmospheric ambient air. This time mismatch effect refers to the time difference between the premature passage of the fast moving atoms ablated from the target, and the shock wave formation and the ablated atoms thereby miss out the shock wave induced thermal excitation process. This was found to be responsible for the weak emission intensities of very light and fast moving analyte atoms such as H and D.[12,13] Taking advantage of the previously reported roles of metastable He excited states in the high pressure He plasma,[12,13] those disturbing effects were effectively eliminated by the appropriately delayed and prolonged detection of the H and D atomic emission. The emission intensities measured during this delayed detection period, were shown to be mainly the result of the so-called He-assisted excitation (HAE) process in the relatively cooled He plasma, via the Penning like ionization process proposed previously.[14] This suggested excitation mechanism was further expounded in most recent studies on the HAE induced emission enhancements observed from other elements.[12,15] Unfortunately, those results were achieved in spectrochemical measurements using orthogonal double pulse configuration with atmospheric He ambient gas.[16] This experimental setup requires the use of two lasers or a single laser with an additional optical system splitting the laser light into two orthogonal beams through two optical paths with very large path length difference using a large number of mirrors in order to create the needed propagation time difference between the two beams as adopted in a previous work.[17] Either one of those requirements would pose a complicated technical problem for its application to in situ inspection of the zircaloy tubes submerged in the cooling water. It hardly offers the much desired practical alternative to the currently adopted method.

In a most recent experiment,[12] the needs of double pulse configuration and high pressure environment was eliminated by employing low-pressure He gas with precleaning of the surface water. This much simpler method was also shown to produced a nice linear calibration line useful for quantitative analysis. Nevertheless, the use of a bulky sample chamber in all the previous cases along with the need of separate surface water precleaning procedure make it virtually inapplicable to in situ H and D detection of zircaloy tubes in the water tank. Therefore, further improvement of the experimental method specifically addressed to overcoming those technical hurdles is badly needed to support the efficient operation and maintenance of both the light and heavy water nuclear reactors.

In this work, the experiment is performed by using a modified small chamber developed previously.[18] In order to simulate the in situ measurement of a zircaloy tube, the chamber is designed to allow the sample surface to be tightly

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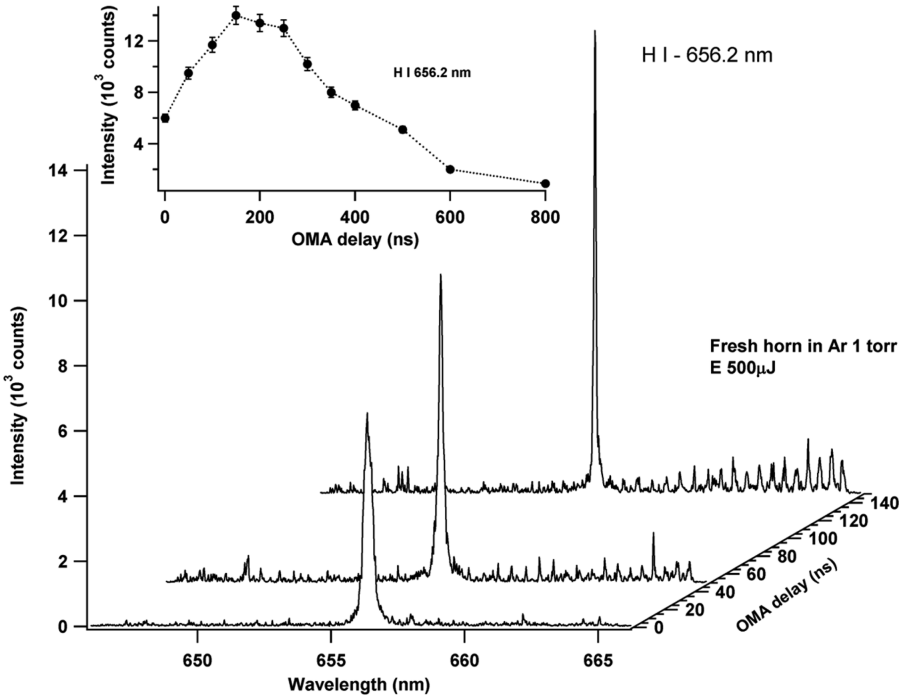

Figure 2. Time-resolved emission spectra of H I 656.2 nm obtained with 500 μJ ps laser radiation and using fresh horn sample in Ar ambient gas at reduced pressure of 0.13 kPa. The gate width of the OMA system is fixed at 10 ns during this measurement.

fitted to the open end of the sample chamber. Besides, in order to minimize the resulted crater size and the interference from surface water, a picosecond Nd:YAG laser is employed and operated at 500 μJ and 300 μJ output energies. At such low irradiation energies, the spectral quality of the emission lines becomes an important issue to be investigated in this study. For this purpose, different ambient gases at various gas pressures as well as different samples are used to examine the excitation mechanism and measure the effect of interfering H emission from the surface water as well as to ascertain the favorable condition needed to achieve the well resolved H and D emission lines arising from the H and D impurity atoms penetrated into a zircaloy tube. Finally, the possible application of this experimental technique to quantitative D analysis with very low detection limit is also explored.

EXPERIMENTAL PROCEDURE

The schematic diagram of the experimental arrangement is depicted in Figure 1 which is similar to the one used in a previous work.[12] In this experiment, however, the picosecond 1 064 nm Nd:YAG laser (Ekspla, PL 2143, 20 ps, maximum energy of 30 mJ) is operated with its output energy varied from 500 μJ to 300 μJ yielding a minimum power density of around 12 TW/cm^2 for 300 μJ energy. The small sample chamber made of quartz tube was specially designed to allow its further development for in situ application in the nuclear power reactor. It has a quartz window on one end for the passage of the laser pulses and an open end on the other side which is equipped with a flat O-ring that can be tightly fitted to the sample surface. The chamber is also equipped with a gas inlet and outlet to allow evacuation of the surrounding gas in the chamber and the continuous flow of the chosen ambient gas at a certain flow rate to maintain the desired gas pressure in the chamber, which is monitored by a digital absolute vacuum meter.

The emission spectrum from the plasma is collected by an optical fiber of 100 μm diameter with its entrance end positioned at a fixed distance of 1 cm sidewise from the plasma beam. The other end of the optical fiber is connected to the detection system consisted of a spectrograph (McPherson, model 2061, f = 100 cm, Czerny Turner configuration) and an optical multichannel analyzer (OMA, Andor ICCD 256 × 1024 pixels). The OMA system is operated at 10 ns gate width and various gate delays for the time-resolved study of the dynamical behavior of the emission intensity. For the measurement of time-integrated intensities, the gate delay and gate width are, respectively, set at 50 ns and 50 μs to cover effectively the entire emission lifetime.

A fresh horn, which is known to have a high concentration of hydrogen and very clean emission spectrum is cut into a sample measuring 30 mm × 30 mm × 10 mm and used in the experiment performed for investigating the basic characteristics of the hydrogen emission in different ambient gases. The pressure dependent intensity variations of the H and D emission lines are also investigated using a porous alumina sample of the same cut doped with 1% D_2O. The measurement is repeated with ambient He and Ar gases at different pressures for the study of interfering effect of surface water molecules. In addition, a set of zircaloy plate of 10 mm × 10 mm cross sectional area and 1 mm thickness are doped with different concentrations of D (60, 170, 540, 600, 700, 900, and 1700 ppm as verified by gas chromatography) are used for verification of the possible existence of a linear calibration line. The sizes of craters created by the microjoule picosecond laser pulses are measured using the digital microscope Keyence (VHX-700).

EXPERIMENTAL RESULTS AND DISCUSSION

The first step in this study is taken to examine the spectral quality of the H emission line and the dynamical behavior of

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the emission induced by the ultra low picosecond laser energy of 500 μJ in the special sample chamber. This is carried out by a time-resolved measurement of the H I 656.2 nm emission intensities from a fresh horn sample in Ar ambient gas at 0.13 kPa. This particular ambient environment is chosen on the basis of a previous experimental results showing the favorable spectral quality of H emission measured from other samples.[12] Figure 2 shows the resulted time dependent intensity variation of the H emission line generated by 500 μJ ps laser pulses and detected with 10 ns gate width of the OMA system. At 5 ns gate delay, the H I 656.2 nm emission line features a relatively broad spectral profile which is narrowing with increasing time delay and becoming very strong and very sharp at 140 ns delay. This is due to the reduction of Stark broadening effect as a result of decreasing electrons produced initially but recombined with the ions subsequently. A detailed variation of the emission intensity over an extended time span is described in the inset. The intensity is seen to reach its maximum at 200 ns and followed by a long decay lasting about 800 ns. This short initial rise and subsequent long decay displayed by the intensity time profile are closely related with the typical excitation and cooling stages in the laser-induced shock wave plasma development process as reported previously.[12] In a separate measurement on the plasma characteristics, the plasma temperature is estimated using the standard two-line method,[12] yielding a temperature of 9000 at the plasma front. Additionally the experiment also gives an estimated electron density of 10^{17} cm^{-3} at the initial stage of the plasma expansion. It shows that even such a low laser energy can generate a shock wave excitation process in Ar ambient gas at the ultra low pressure and produces the sharp plasma emission presented in the inset of Figure 2.

In the following experiment, the pressure dependent intensity variations of H I 656.2 nm emission line are measured in different ambient gases of air and Ar for comparison, since the pressure dependent intensity variations were known to be sensitively affected by the kind of ambient gas used in LIBS.[12] These effects are closely related with the shock wave plasma characteristics such as its strength, speeds of its formation and the plasma front propagation. All of these are in turn influenced by the multicollision processes between the ablated atoms and the surrounding gas molecules. The resulted strong gas compression is understood to give rise to the plasma shock wave. The following conversion of kinetic energy to the high-temperature thermal energy is responsible for the thermal excitation and the subsequent emission process. Therefore, different ambient gases and gas pressures (or gas densities) are likely to have different influences on the induced emission characteristics. These different effects are investigated in the following experiment using a laser energy of 500 μJ and with the OMA system operated at 10 ns gate delay and 50 μs gate width. Described in Figure 3 are the results obtained with ambient (a) air and (b) Ar gas. As shown in Figure 3a, the maximum emission intensity of H I 656.2 nm in ambient air is found in the very low pressure regime of around 0.2 kPa, followed by its rapid decline with increased air pressure. This peculiar pressure dependent on H emission intensity is due to the time mismatch between the passage of the fast moving ablated H atoms and the slower formation of the plasma shock wave induced by the heavier host elements as previously reported.[19] A qualitatively similar pressure dependent intensity variation is also found in Ar ambient gas as shown in Figure 3b with nonetheless much higher intensity, roughly 10-fold of that presented in Figure 3a. The pressure dependent intensity

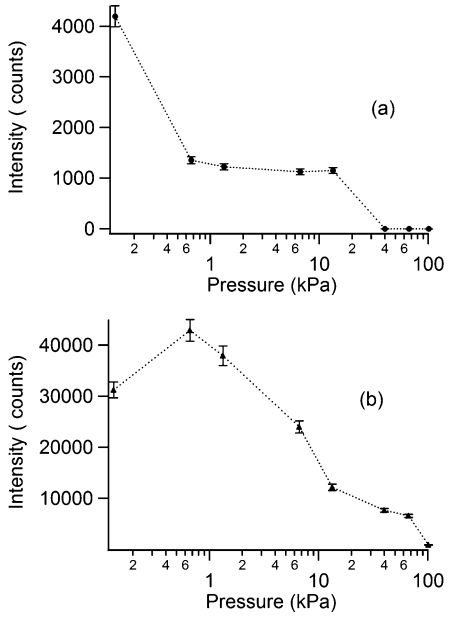

Figure 3. Pressure dependent intensity variation of H I 656.2 nm in ambient (a) air and (b) Ar gas. A picosecond laser radiation of 500 μJ is focused onto a fresh horn sample with 50 ns gate delay and 50 μs gate width.

measured in He ambient gas (not shown in the figure) also shows the same pattern of variation with its intensity lying between the two cases presented in the figure.

Apart from the advantage of higher emission intensity provided by Ar ambient gas, it is also important to examine in this ambient gas the possible interference of D emission by the H emission line having a wavelength difference of only 0.18 nm from the D emission line. The interfering H emission mentioned above is the emission line having its origin in the H atoms dissociated from the ubiqitous water molecules on the sample surface. This long-standing problem has been copied with a variety of special pretreatments,[12] which are inapplicable to the case under consideration. This unwanted effect is investigated by using a porous alumina doped with 1% of D_2O for the simultaneous measurement of pressure dependent intensity variations from the D dopant and the hydrogen dissociated from the surface water. Different ambient gases at different pressures are employed for comparison. Presented in Figure 4 are the emission spectra obtained with the OMA system operated at 10 ns gate delay and 50 μs gate width in ambient He gas of (a) 98.8 kPa and (b) 2.6 kPa. It is seen from Figure 4a that the D and H emission lines are broadened and completely mixed up and practically swamped in the noise confirming the unfavorable emission in higher ambient gases shown in Figures 2 and 3. Meanwhile the spectrum in Figure 4b reveals a sharp D line with the H emission appearing as a tiny signal adjacent to the D emission line in the low-pressure plasma without interfering the D signal. It is worthwhile to note that the poor spectral quality indicated by the low S/N ratio in Figure 4a for atmospheric He ambient gas may seem to contradict the result reported previously.[12,13,16] However, it must be noted that a much lower energy is used in the present experiment. In view of the highest H emission intensity obtained with Ar ambient gas as shown in Figure 3, the measurement is repeated with the He gas replaced by Ar ambient gas at various pressures. The result is presented in Figure 5. One does observe that the emission intensity of D

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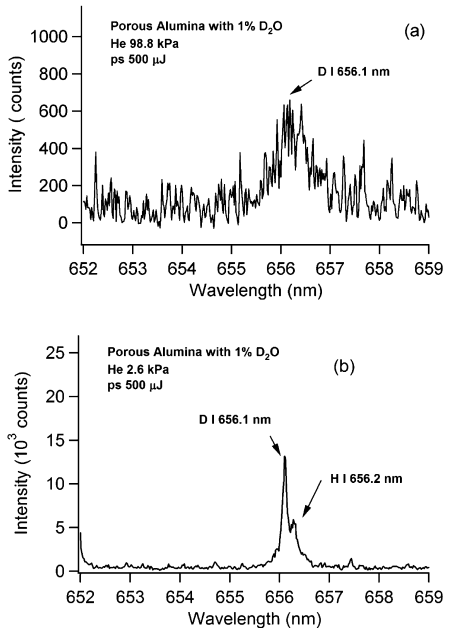

Figure 4. Emission spectrum generated in ambient helium gas at (a) 98.8 kPa and (b) 2.6 kPa by a picosecond laser radiation of 500 μJ on a porous alumina sample containing 1% of D_2O with 50 ns gate delay and 50 μs gate width.

increases with decreased gas pressure, and the highest intensity attained at 0.13 kPa is almost 3× the intensity detected in He ambient gas shown in Figure 4, in agreement with the result mentioned earlier referring to Figure 3. The enhanced emission intensities shown in Figures 4 and 5 at reduced gas pressures were already reported previously in different ambient gases.[12] It is understood as the result of reduced time mismatch between the premature fast passage of the light ablated atoms and the delayed formation of the plasma shock wave at high gas pressure. At lower gas pressure, the formation of the shock wave is known to take place at a faster pace and hence reduces the adverse time mismatch effect. Again, the appearance of the tiny H emission signal has virtually no interfering effect on the D emission at 0.13 kPa gas pressure. It is remarkable that the suppression of the unwanted surface water effect can be so simply and effectively achieved without relying on the usually adopted treatment of preheating the chamber and laser precleaning of the sample surface or even the use of double pulse configuration.[12,13,15]

The appearance of the tiny H emission signal is nevertheless an important indication of the possibility of simultaneous detection of H and D emission lines from the zircaloy penetrated by both H and D atoms during the operation of the nuclear reactor. For this case, the resolution of these two lines which are separated by a mere 0.18 nm wavelength must be examined and clearly verified. This is carried out by repeating the preceding measurement using a zircaloy plate doped with 50 ppm of H and 600 ppm of D. The result is presented in Figure 6. One sees that the fully resolved spectral lines of D and H with the highest intensities are obtained with Ar ambient gas at 0.13 kPa. The advantage of low gas pressure is further verified by measuring the pressure dependent intensity variation of D I 656.1 nm emission line described by the result presented in Figure 7. The D emission is seen to attain its maximum intensity at the very low gas pressure of about 0.13 kPa, which is followed by its rapid decrease with increased Ar

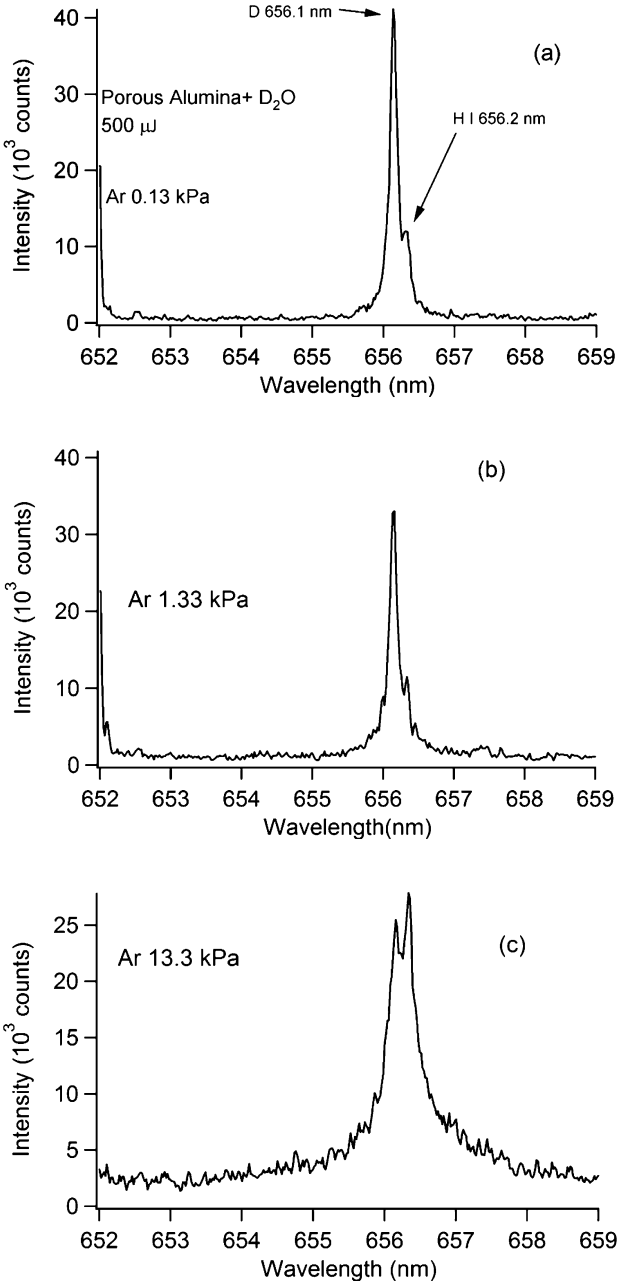

Figure 5. Emission spectrum from the same D_2O doped porous allumina sample in Figure 4 generated in ambient argon gas at various pressures by picosecond laser radiation of 500 μJ. The gate delay and gate width of the OMA system are fixed at 50 ns and 50 μs, respectively.

gas pressure similar to the pressure dependent intensity variations of H I 656.2 nm emission presented earlier in Figure 3.

Given the well resolved D and H emission lines, a further experiment is conducted to examine the possibility for quantitative analysis of D. For this purpose, a series of zircaloy samples are prepared with different concentrations of D impurity. Meanwhile the same experiment is repeated with stepwise reduced irradiation energies. It is found that the same spectral quality of D emission is achieved with the irradiation energy lowered down to 300 μJ. This energy is then employed for the following measurements of the D emission intensities of those samples with the expectation of minimizing the resulted

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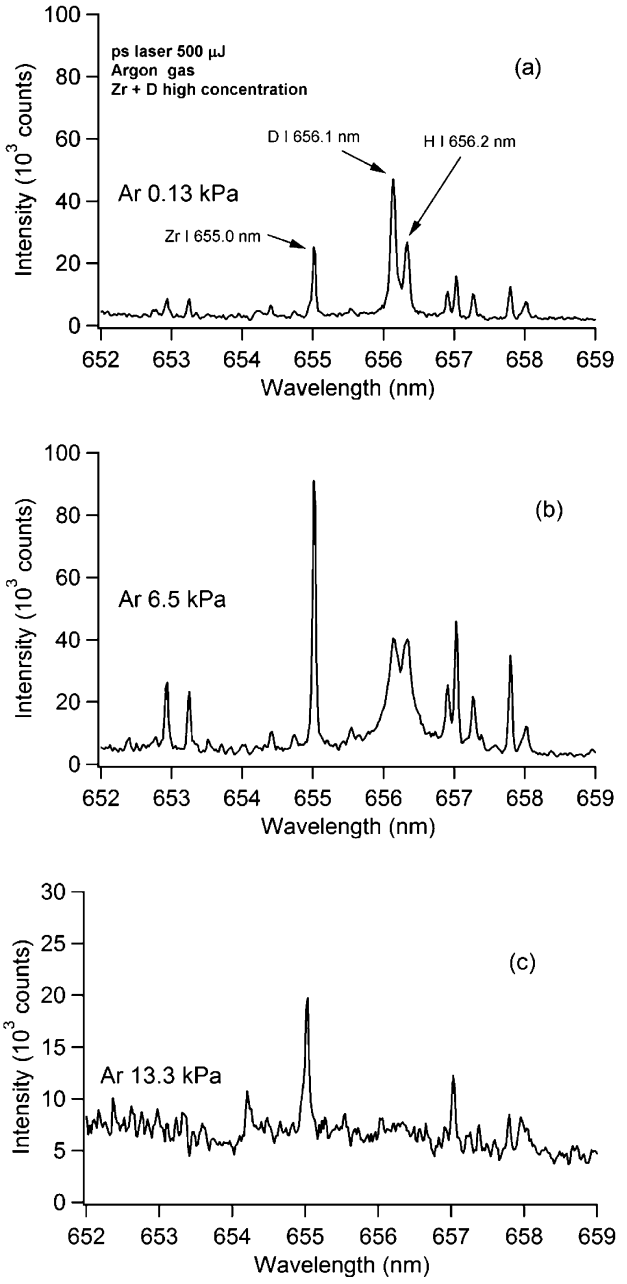

Figure 6. Emission spectra generated in ambient argon gas at various pressures by picosecond laser radiation of 500 μJ on a zircaloy plate containing 600 ppm of deuterium and 50 ppm of hydrogen. The gate delay and gate width of the OMA system are fixed at 50 ns and 50 μs, respectively.

crater size. The resulted plot of D I 656.1 nm emission intensity as a function of the corresponding D concentration is presented in Figure 8, where the measured D emission intensity is normalized by the Zr emission intensity appearing in each case. Each data point in this figure is the average of data produced by 50 successive laser shots on the same sample spot. This measurement is then repeated on five different spots of the same sample. The results of these measurements are found to be highly reproducible, implying the high uniformity of the D impurity distribution in the sample. The resulted intensity-concentration plot is seen to exhibit a nice linear relationship with practically extrapolated zero intercept. The limit of detection (LOD) for D is estimated from the emission

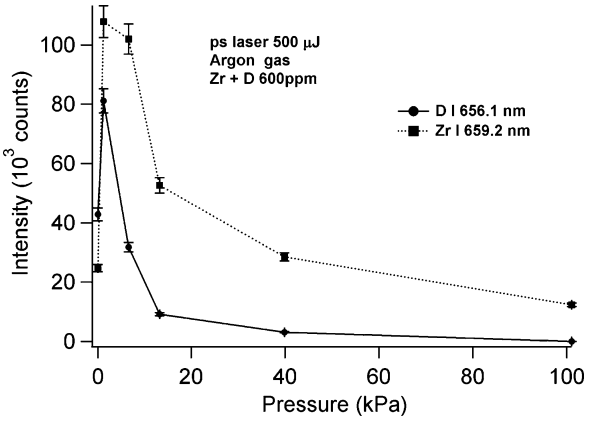

Figure 7. Detailed pressure dependent intensities of D I 656.1 nm and Zr I 659.2 nm emission lines from zircaloy plate containing 600 ppm of D produced by 500 μJ ps laser pulses with 50 ns gate delay and 50 μs gate width.

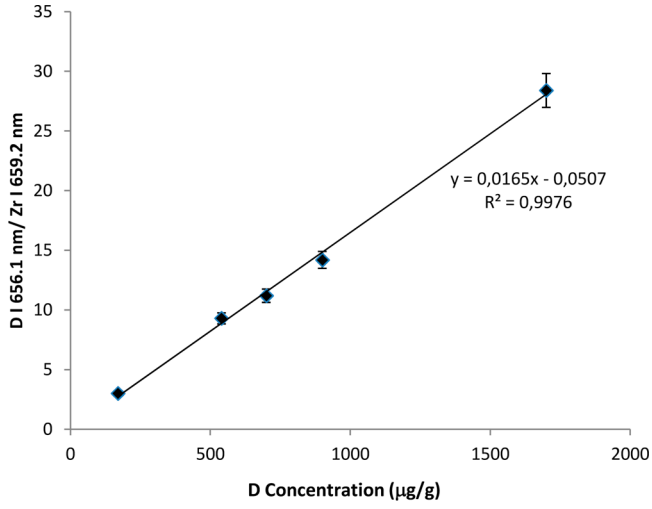

Figure 8. Calibration curve for deuterium in zircaloy plate, obtained by picosecond laser irradiation of 300 μJ on a zircaloy plate containing different concentrations of deuterium with 50 ns gate delay and 50 μs gate width.

spectrum of a zircaloy-4 sample containing 300 ppm D impurity following the conventional criterion as a ratio of the signal against 3 times the surrounding noise level. The resulted LOD is found to be less than 10 ppm (8.9 ppm), which is well below the commonly accepted maximum threshold of 800 ppm for nondetrimental D concentration in the zircaloy tube.

Finally, the additional and important advantage of minimal destructive effect offered by the use of very low laser energy is clearly verified by the tiny crater of about 5 μm diameter and 25 μm in depth as shown by the photo presented in Figure 9.

CONCLUSION

We have demonstrated in this study the viability of spectrochemical analysis of D and H impurities with picosecond laser pulses of 300 μJ output energy in 0.13 kPa Ar ambient gas using a small and specially designed sample chamber. The results show the effective suppression of the interfering effect from surface water molecules on the one hand, while demonstrating on the other hand the fully resolved D I 656.1 nm and H I 656.2 nm emission lines from D and H impurities in the zircaloy sample. The results further exhibit a

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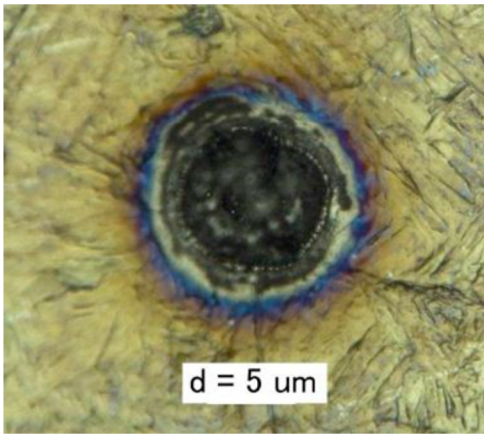

Figure 9. Photo of crater created by 50 shots of 300 μJ laser pulses which is taken by the digital microscope and further measured for its depth by a stylus.

linear calibration line with extrapolated zero intercept promising for quantitative analysis. Finally, the use of the extremely low laser energy has resulted in a minimum destructive effect featuring average crater size of about 5 μm in diameter and 25 μm in depth. These results clearly suggest the potential development of a practical analytical tool for in situ inspection of zircaloy tubes in heavy water nuclear power plants. It goes without saying, however, that the ultimate realization of in situ application of this technique to zircaloy tube inspection in the reactor implies the need of performing the measurement with the zircaloy tubes remaining in the heavy water tank, preferably without disturbing the reactor operation. Work in this direction is being pursued, and the result will be reported elsewhere.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Freidberg, J. P.; Kadak, A. C. *Nat. Phys.* **2009**, *5*, 370−372.

(2) Suyanto, H.; Lie, Z. S.; Niki, H.; Kagawa, K.; Fukumoto, K.; Hedwig, R.; Abdulmadjid, S. N.; Marpaung, A. M.; Pardede, M.; Suliyanti, M. M.; Hidayah, A. N.; Jobiliong, E.; Lie, T. J.; Tjia, M. O.; Kurniawan, K. H. *Anal. Chem.* **2012**, *84*, 2224−2231.

(3) Miziolek, A. W., Palleschi, V., Schechter, I. *Laser-Induced Breakdown Spectroscopy*; Cambridge University Press: Cambridge, U.K., 2006.

(4) Cremers, D. A., Radziemski, L. J. *Handbook of Laser-Induced Breakdown Spectroscopy*; Wiley: New York, 2006.

(5) Takahashi, T.; Thornton, B.; Sato, T.; Ohki, T.; Ohki, K.; Sakka, T. *Spectrochim. Acta, Part B* **2016**, *124*, 87−93.

(6) Nishijima, D.; Hollmann, E. M.; Doerner, R. P. *Spectrochim. Acta, Part B* **2016**, *124*, 82−86.

(7) Novakova, H.; Hola, M.; Vojtisek-Lom, M.; Ondracek, J.; Kanicky, V. *Spectrochim. Acta, Part B* **2016**, *125*, 52−60.

(8) Michel, A. P. M.; Sonnichsen, F. *Spectrochim. Acta, Part B* **2016**, *125*, 177−183.

(9) Skocic, M.; Bukvic, S. *Spectrochim. Acta, Part B* **2016**, *125*, 103−110.

(10) Brech, F.; Cross, L. *Appl. Spectrosc.* **1962**, *16*, 59−61.

(11) Loree, T. R.; Radziemski, L. J. *Plasma Chem. Plasma Process.* **1981**, *1*, 271−280.

(12) Kurniawan, K. H.; Tjia, M. O.; Kagawa, K. *Appl. Spectrosc. Rev.* **2014**, *49*, 323−434.

(13) Hedwig, R.; Lie, Z. S.; Kurniawan, K. H.; Chumakov, A. N.; Kagawa, K.; Tjia, M. O. *J. Appl. Phys.* **2010**, *107*, 023301.

(14) Lie, Z. S.; Niki, H.; Kagawa, K.; Tjia, M. O.; Hedwig, R.; Pardede, M.; Jobiliong, E.; Suliyanti, M. M.; Abdulmadjid, S. N.; Kurniawan, K. H. *J. Appl. Phys.* **2011**, *109*, 103305−1−4.

(15) Suliyanti, M. M.; Hidayah, A. N.; Pardede, M.; Jobiliong, E.; Abdulmadjid, S. N.; Idris, N.; Ramli, M.; Lie, T. J.; Hedwig, R.; Tjia, M. O.; Kurniawan, K. H.; Lie, Z. S.; Niki, H.; Kagawa, K. *Spectrochim. Acta, Part B* **2012**, *69*, 56−60.

(16) Suyanto, H.; Lie, Z. S.; Niki, H.; Kagawa, K.; Fukumoto, K.; Rinda, H.; Abdulmadjid, S. N.; Marpaung, A. M.; Pardede, M.; Suliyanti, M. M.; Hidayah, A. N.; Jobiliong, E.; Lie, T. J.; Tjia, M. O.; Kurniawan, K. H. *Anal. Chem.* **2012**, *84*, 2224−2231.

(17) Wang, X. D.; Michalowski, A.; Walter, A.; Sommer, S.; Kraus, M.; Liu, J. S.; Dausinger, F. *Opt. Laser Technol.* **2009**, *41*, 148−153.

(18) Lie, T. J.; Kurniawan, K. H.; Hedwig, R.; Pardede, M.; Tjia, M. O.; Idris, N.; Kobayashi, T.; Lee, Y. I.; Kagawa, K. *Jpn. J. Appl. Phys.* **2005**, *44*, 202−209.

(19) Lie, Z. S.; Tjia, M. O.; Hedwig, R.; Suliyanti, M. M.; Abdulmadjid, S. N.; Idris, N.; Marpaung, A. M.; Pardede, M.; Jobiliong, E.; Ramli, M.; Suyanto, H.; Fukumoto, K.; Kagawa, K.; Kurniawan, K. H. *J. Appl. Phys.* **2013**, *113*, 053301.

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