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論文審査の結果の要旨

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学位論文題目

Development of advanced elemental detection methods in particles and gases using laser-induced breakdown spectroscopy and laser breakdown time-of-flight mass spectrometry for the application to thermal and nuclear power plants

火力及び原子力プラント応用のためのレーザ誘起ブレークダウン法及びレーザガスブレークダウンＴＯＦＭＳ法を用いた粒子及びガス中の元素組成計測技術の開発

審査結果の要旨

環境保全の観点から，火力プラントや原子力プラントにおけるガス中の重金属成分や放射性物質をモニタリングするニーズが拡大している．従来，これらの成分の検知では，長時間サンプリングを行った後，濃縮・化学分析を行う手法が適用されている．しかしながら，これらの方法では，ガス中の重金属成分や放射性物質を検知するまでに数日から数週間を要していた．本研究ではガス中の重金属成分や放射性物質をリアルタイムに検知できる方法として，「レーザ誘起ブレークダウン法」及び「レーザブレークダウン飛行時間型質量分析法」の高度化を図った．レーザ誘起ブレークダウン現象において，プラズマによる原子化現象過程を解析し，減圧下及び短パルスレーザ照射における新たな現象を見出し、計測の高感度化、計測対象拡大などの成果を得た．また，実験的検証を通して，火力プラントや原子力プラントへの適用性を評価した．

以上，本研究は，微量元素成分をリアルタイムにモニタリングする新しいコンセプトの計測技術を提案すると共に，その実験的検証を提示するものであり，本論文は博士（工学）の学位授与に値するものと判定する。

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論 文 内 容 要 旨

報告番号	甲 先 第 **196** 号	氏 名	王 珍珍
学位論文題目	Development of advanced elemental detection methods in particles and gases using laser-induced breakdown spectroscopy and laser breakdown time-of-flight mass spectrometry for the application to thermal and nuclear power plants 火力及び原子力プラント応用のためのレーザ誘起ブレークダウン法及びレーザガスブレークダウンＴＯＦＭＳ法を用いた粒子及びガス中の元素組成計測技術の開発		

内容要旨

In order to simulate coal combustion and develop optimal and stable boiler control systems in real power plants, it is imperative to obtain the detailed information in coal combustion processes as well as to measure species contents in fly ash, which should be controlled and analyzed for enhancing boiler efficiency and reducing environmental pollution. The fly ash consists of oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, and so on), unburned carbon, and other minor elements. Recently Laser-Induced Breakdown Spectroscopy (LIBS) technique has been applied to coal combustion and other industrial fields because of the fast response, high sensitivity, real-time and non-contact features. In these applications it is important to measure controlling factors without any sample preparation to maintain the real-time measurement feature. The relation between particle content and particle diameter is also one of the vital researches, because compositions of particles are dependent on their diameter. In this study, we have detected the contents of size-segregated particles using LIBS. Particles were classified by an Anderson cascade impactor. The plasma conditions such as plasma temperature are dependent on the size of particles and these effects must be corrected to obtain quantitative information. The plasma temperature was corrected by the emission intensity ratio from the same atom. Using this correction method, the contents of particles can be measured quantitatively in fixed experimental parameters. This method was applied to coal and fly ash from a coal-fired burner to measure unburned carbon and other contents according to the particle diameter. The CO_2 effect was also discussed to accurately evaluate unburned carbon in fly ash in exhausts. The acquired results demonstrate that the LIBS technique is applicable to measure size-segregated particle contents in real time and this method is useful for the analysis of coal combustion and its control because of its sensitive and fast analysis features.

It has been highly recognized heavy metals and other trace species pollution concerns the environment, as well as human health. This paper describes the rapid detection of trace species such as mercury and iodine using low pressure laser-induced breakdown spectroscopy (LIBS) and laser breakdown time-of-flight mass spectrometry (LB-TOFMS) at improved sensitivity. One of the challenging targets of LIBS is the enhancement of detection limit. In this study, the detection limit of gas phase LIBS analysis has been improved by controlling the pressure and laser pulse width. In order to verify this method, low pressure gas plasma was induced by nanosecond and picosecond lasers. Several trace species of Hg, iodine, Cs, Sr and so on were measured using low pressure LIBS. For example, the method was applied to the detection of mercury (Hg), and the emission intensity ratio of Hg atom: I_{Hg} to NO emission signal: I_{NO} (interference signal), which was formed during the plasma generation and cooling process of N_2 and O_2 in the air, was analyzed to evaluate LIBS detection limit. It was demonstrated that the enhancement of I_{Hg}/I_{NO} arose by decreasing the pressure to a few kPa and I_{Hg}/I_{NO} of picosecond breakdown was always much higher than that of nanosecond breakdown at low buffer gas pressure. The measurement results of iodine in N_2 demonstrated that low-pressure LIBS is the favourable method for trace species measurement in analytical application. The plasma generation process can be controlled by the pressure and laser pulse width for the larger ionization and excitation processes of iodine, which was discussed by the intensity ratio of iodine emission at 183 nm to nitrogen emission at 174.3 nm. The buffer gas effect was also discussed by the measurements of Hg and iodine in different buffer gases of air and N_2. The Hg detection limit in air of nanosecond breakdown was 450 ppb ($3\sigma/m_s$) at 700 Pa. According to the enhancement of picosecond breakdown at low pressure, the detection limit was evaluated to be 30 ppb ($3\sigma/m_s$) in picosecond (35 ps) breakdown at 700 Pa. the detection limit can be enhanced when employing the buffer gas of N_2. The detection limit of iodine in N_2 was 60 ppb ($3\sigma/m_s$) in nanosecond breakdown at pressure of 700 Pa. there was not evident enhancement of iodine detection limit employing short pulse width breakdowns. The detection limit of iodine in air became worse due to the high quenching rate of excited iodine in buffer gas of air.

In the measurements of Hg and iodine using LB-TOFMS, two irradiation wavelengths of 1064 nm and 532 nm were employed under various experimental conditions without partial fragmentation interference from other species. The second harmonic 532 nm performs excellent measurement results. The influence of pressure on signal intensity displays a linear growth when increasing the pressure. The power dependence shows that as the laser power increased, mercury ion and iodine ion signal intensity increased first and then decreased. Experiment with different buffer gases clarified the recombination of mercury ion and iodine ion with electrons when increasing the laser power, resulting in the decrease of mercury ion and iodine ion signal intensity. Mercury ion signal intensity can

be enhanced 3.8 times and the signal intensity of iodine ion can be enhanced 1.3 times employing 35 ps 532 nm breakdown. The detection limits ($3\sigma/m_s$) of mercury ion and iodine ion signal using 35 ps laser breakdown were 0.82 ppb and 6.18 ppb respectively.