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論　文　内　容　要　旨

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学位論文題目	Study on the long-short double-pulse laser-induced breakdown spectroscopy for the steel chemical composition analysis (鉄鋼化学組成分析におけるロング・ショートダブルパルスレーザ誘起ブレークダウン法の研究)		

内容要旨

Recently, various spectral analysis methods are studied and applied to the steel composition measurement, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy (AAS), spark optical emission spectroscopy (S-OES), laser-induced breakdown spectroscopy (LIBS). Among these spectral methods, LIBS is considered to be a good method that can be applied in the on-line detection of steel composition during making process. LIBS technique is highly anticipated because of the fast response, high sensitivity, real-time and non-contact features. For the online analysis, it is important to measure controlling factors without any sample preparation to maintain the real-time measurement feature. In this study, we have discussed the potential application fields of LIBS. With the rapid development of the modern industry, a lot of techniques have been studied for the industrial production. These advanced techniques also bring a requirement of process analysis and raw material quality control. The joint research of LIBS with other advanced techniques is meaningful for the performance improvement of industrial production. For the advanced forming production line, the quality of the steel part after forming is important for the process. LIBS technique is a promising method to analyze the formed steel parts on the production line. For the production of electrical machine of vehicle, LIBS can be applied to the quality control of the raw silicon steel plate which is one of the most important raw material for the rotor and stator of the electrical machine. LIBS technique also has a promising future in the fields of the online rapid analysis of aluminum sheet for the plastic joint process, the analysis and control of the steel making process, the waste disposal and recycling plant. According to these potential industrial applications of LIBS, the study on the analysis of manganese in steel samples were carried out in this dissertation. A new LIBS method named as long-short double-pulse LIBS (DP-LIBS) method is developed in this study for the application of real plants.

Firstly, the steel samples at solid state were measured to investigate the performance improvement of the long-short double-pulse LIBS. The role of inter-pulse delay in signal enhancement for long-short DP-LIBS was investigated

by experiments, the results showed that the optimal coupling of pre-heating and re-heating effects can be obtained by firing the short pulse at the middle of long pulse. Compared with SP-LIBS, long-short DP-LIBS has obtained 3-7 folds signal enhancement in the optimal inter-pulse delay. Through the observation of plasma, the plasma images showed the remarkable differences between SP-LIBS and long-short DP-LIBS. The plasma was bigger and had a longer lifetime in long-short DP-LIBS condition. Moreover, the observed images of long pulse LIBS suggested that the long pulse can't generate the plasma due to the low power density. The variation of plasma temperature showed that the plasma was maintained at a high and stable temperature. The variation of time-resolved intensity ratio was different for SP-LIBS and long-short DP-LIBS. I_{Mn}/I_{Fe} linearly increased with delay time in SP-LIBS condition, whereas, it showed a remarkable stabilization around the delay time of 3000 ns in long-short DP-LIBS condition. These phenomena indicated that the plasma was stabilized by using the long-pulse-width laser beam. Through the testing at different sample temperatures, the measured spectra were consistent for long-short DP-LIBS, whereas, the spectra were significantly different for SP-LIBS. The results demonstrated that long-short DP-LIBS can be used for the online measurement of steel production line, in where the temperature of target is unknown.

For the quantitative analysis of steel samples under the simulated plant conditions, the long-short DP-LIBS method also show an acceptable performance. The long pulse made it possible to obtain clear spectra from the steel washers which had an obvious rusty layer. Through the study on the crater morphology, the improvement of detection ability can be attributed to the cleaning effect of long pulse. This result indicated that long-short DP-LIBS can be used in steel production lines, in where severe oxidation is difficult to be avoided. The emission intensity was obviously enhanced by long-short DP-LIBS because of the preheating effect of the long pulse. The comparison of spectra showed that more spectral lines were available for quantitative analysis from the spectrum of long-short DP-LIBS. This result suggested that long-short DP-LIBS can obtain more spectral information under the same experimental conditions. The measured results of long-short DP-LIBS showed a better linearity. The determination coefficients (R^2) was 0.988 for the calibration curve of long-short DP-LIBS, which is acceptable for the industrial application. Moreover, the larger slope of calibration curve for long-short DP-LIBS indicated that the effect of self-absorption was eliminated by the long pulse, which therefore improved the analytical performance of LIBS. The prediction results showed that the precision and accuracy of long-short DP-LIBS were better than those of SP-LIBS. The mean RSD% was reduced from 29.3% to 10.5% and the mean REP% was reduced from 94.9% to 4.9%.The improvement can be attributed to the stabilized plasma which was generated by long-short DP-LIBS process. The simulated prediction experiments demonstrated that the analytical performance of LIBS can be improved by adding a long puls

e to the traditional SP-LIBS. The measurement results of liquid steel showed that the conventional SP-LIBS can't obtain a satisfied calibration curve due to the unstable sample condition. However, long-short DP-LIBS showed an acceptable performance for the measurement of liquid steel samples. The fitting parameters R^2 of the calibration curve is 0.9788 for the long-short DP-LIBS, which is only 0.5329 for the SP-LIBS. At the same time, the standard deviation of the measured intensity ratio values are relative low in the long-short DP-LIBS results. It proved that the plasma is stabilized by the long pulse laser beam.