Rapid Inspection of Defects of Steel by Laser Induced Breakdown Spectroscopy

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Abstract

A rapid and simple technique has been developed for inspection of defects of steel using laser induced breakdown spectroscopy (LIBS). Irradiation from a Q-switched Nd:YAG laser was focused onto the sample surface by a plano-convex lens with a spot diameter of about 1mm to ablate a portion of sample and generate a micro plasma. Emission from the plasma was transmitted by a fiber optics to a Paschen-Runge mounting polychrometer. Each sample was analyzed at two points, normal and defect parts and these two analytical results were compared with each other. Typical elements could be detected at defect part with significantly high intensities for different types of inclusion; Al for alumina, Al, Ca, Mg, Si, Na for mold flux and Al, Ca, Mg for slag. Therefore, type of non-metallic inclusion causing the defect could be attributed by LIBS. An evaluation time was within 30 minutes including sample preparation. The developed method was also applied to elemental mapping of central segregation of slabs.

1. Introduction

Defects in steel materials adversely affect the quality and yield of products constructed from them. Therefore, in steelmaking processes, developing a technology that permits speedy determination of the causes of defects is as important as developing equipment technology related to defect prevention, such as continuous casting that applies an electromagnetic stirrer and a level magnetic field to control surface defects and center segregations.1)

Surface defects in rolled steel are not limited to mechanical defects, including roll marks. There are various other surface defects: mold flux-induced defects ascribable to the penetration into steel of the mold flux added as mold lubricant in the continuous casting process; alumina-induced defects due to nonmetallic inclusions in steel caused by excessive oxidation and outflow of converter slag into the ladle in the refining process or insufficient floating of alumina in the vacuum degassing equipment (RH); and slag-induced defects resulting from nonmetallic inclusions ascribable to the entanglement of slag in the tundish. In addition, there are defects ascribable to insufficient removal of scale from the steel surface after operation of the reheating furnace. It is important to speedily investigate the cause of each of these defects and identify which manufacturing process needs to be corrected.

Once the cause of a specific defect is identified, it is possible to implement suitable remedial measures without delay. Examples of them are stabilization of the mold bath level and optimization of the electromagnetic stirrer of the mold bath for mold flux-induced defects; prevention of excessive decarburization of steel in the converter, improvement of the quality of slag, and/or taking a suitable circulation time after RH deoxidation for alumina-induced defects; ensuring of sufficient time for slag to float in the tundish for slag-induced defects; and optimization of the reheating furnace tempera-

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ture, enhancement of the descaling capacity, etc. for scale-induced
defects.

Concerning center segregations that can occur during solidifica-
tion of a slab, there are concerns that they will be carried over to the
product in the form of internal defects in the steel sheet. Therefore, if
center segregations could be detected as a slab is being cast, impru-
dent use of the material can be avoided, resulting in making the most
effective use of it.

So far, various methods have been used to investigate the causes
of defects in steel. For surface defects, cross sections of defective
parts are observed using optical microscopy and EPMA (electron
probe micro-analysis) or EDX (energy-dispersive X-ray spectro-
copy). Center segregations are observed by means of macroscopic
examination by etching, etc. These and other conventional meth-
ods require complicated and time-consuming preparation of the
sample (e.g., cutting and polishing). Besides, they are not very reli-
able because the substance that is the cause of the defect might come
off the sample during sample preparation or it might be overlooked
during observation of a specific cross section of the sample. There-
fore, the results of investigations using them would hardly be able to
be fed back to manufacturing operations speedily and properly.

As new techniques to swiftly investigate the causes of defects,
there is laser ablation ICP (inductively coupled plasma) emission
spectrometry and elemental mapping by spark emission spectrom-
etry. It has been reported that both methods are very effective for
examining surface defects in steel sheet. However, laser ablation ICP
emission spectrometry requires a somewhat complicated system,
which is rather difficult to operate and maintain. On the other hand,
elemental mapping by spark emission spectrometry, which utilizes a
spark discharge, requires delicate control at the point of discharge
according to the sample shape and structure.

Laser-induced breakdown spectroscopy (LIBS) is an analytical
technique to obtain information about elements in the target sub-
stance by observing the emission lines of wavelengths specific to
each element that are emitted in the process of relaxation of atoms
that are collision-excited by electrons, etc. in hot plasma generated
by a laser pulse with a high peak power. Since LIBS does not
require any special chemical pretreatment, sample preparation is easy
and limitations on the sample shape are relatively modest. The main
devices required for LIBS are a laser and a spectrometer. Therefore,
it is possible to configure a compact LIBS system. Besides, LIBS
does not require special skill.

Examples of elemental mapping implemented using LIBS include:
mapping of MnS in steel sheet; mapping of nonmetallic inclusions
on the surface of stainless steel sheet by laser line scanning; mapping
of inclusions in aluminum alloy; etc. As examples of depth profiling,
there is LIBS analysis of plating layers. However, none of the above studies was conducted from the standpoint of determin-
ing the causes of defects. In the present study, we discussed the pos-
sibility of applying LIBS to speedily determine the causes of defects
and analyze center segregations in steel focusing our attention on the
advantageous characteristics of LIBS, which does not require bur-
densome chemical or physical pretreatment.

2. Experimental

2.1 Experimental apparatus

The experimental apparatus is presented schematically in Fig. 1.
A Q-switched Nd:YAG laser beam (Continuum Surelite III-10; wave-
length: 532 nm, pulse width: 12 ns, pulse repetition frequency: 10
Hz), focused by a plano-convex lens having a focal length of 80 mm,
was irradiated onto the surface of the sample to generate micro-plasma
by evaporating and atomizing part of the sample. The spot diameter
at the sample surface was about 1 mm, and the pulse energy was 100
mJ. Emissions from the plasma were transmitted over an optical fi-
ter cable to a Paschen-Runge polychrometer (Shimadzu Corpora-
tion; focal length: 500 mm) for spectroscopic measurement. Detected
photo intensities were integrated with a delay time of 10 ms against
the laser pulse. We paid special attention to elements composing
nonmetallic inclusions. The analytical lines for these elements are
shown in Table 1.

Fig. 2 shows the Al calibration curve we prepared using JSS-
certified reference materials with our LIBS system. The linearity of
the calibration line was good in the range from 10 to 780 g/g-Al.
From this, we could confirm that it would be possible to quantita-
tively evaluate the difference in element concentration in the sample.

![Fig. 1  Schematic diagram of LIBS system](image-url)
2.2 Samples and analytical method
(1) Surface defects of steel sheets
We analyzed four galvanized sheets (Samples A, B, C, and D) whose surface defects could be observed with the unaided eye. Each of the samples was fixed on the X-Y stage inside the laser irradiation chamber, which was filled with atmospheric Ar. As shown in Fig. 3, both the normal and the defective parts were analyzed and the results were compared. In order to verify the analysis results obtained by LIBS, we observed cross sections of the defective parts by EPMA and compared them.

(2) Sample with center segregation
A sample containing center segregation was cut out from a slab of low-alloy steel. The segregated part of the sample was previously confirmed by the etching method. After the etched layer of sample surface was belt-polished, it was analyzed.

In the experiment, while the sample fixed to the X-Y stage was scanned, the laser beam was irradiated onto points of 18 × 8 at pitches of 1 mm (300 pulses per point) for semi-quantitative mapping of element concentrations at the sample surface. It was considered that more C, S, Mn, and P, having a small solid-liquid partition coefficient, would be concentrated in the center-segregated part than other elements. In the present experiment, therefore, we assumed C and S to be elements that are easily concentrated, and Si, Al, and Ca to be elements that are reluctantly concentrated.

3. Experimental Results and Discussion
3.1 Surface defects of steel sheets
The emission intensities of Si, Al, and Ca obtained by analyzing the normal part (〇) and defective part (×) of each of Samples A, B, and D are shown in Figs. 4 (i), (ii), and (iii). Each of the measured values shown in Fig. 4 is an integral intensity for 300 pulses, which has been normalized by the averaged values obtained by analyzing the normal part several times. As shown in Fig. 4 (i), in Sample A, Ca was clearly detected in the defective part. Si and Al also showed rather strong emissions in the defective part of the sample.

The above results suggest that CaO exists in the defective part of Sample A. CaO is contained in both mold flux and slag. Looking at Fig. 4 (ii), on the other hand, in Sample B, there is very little difference in Ca intensity between the normal and the defective parts, whereas only Al was strongly detected in the defective part. Concerning Sample D, as shown in Fig. 4 (iii), there was little difference in the intensity of Si, Al, or Ca between the normal and the defective parts. Therefore, it was assumed that the defect in Sample D was a scale defect, that is, an oxide film remaining on the sheet surface.

The emission intensities for each of Na, Mg, Al, Si, Ca, Zn, and Fe per pulse measured by irradiating a laser beam to the normal and
defective parts of Sample A are shown in Figs. 5 (i) and (ii). In the
defective part, the intensities of Na, Mg, and Ca are much higher
than those in the normal part. Since these elements are characteristic
of mold flux, the defect in Sample A was judged to be caused by
mold flux entrapped in the steel during casting. It should be noted
that in the present analysis method, it is unnecessary to remove the
sheet of the plating layer, which is naturally removed during irradia-
tion by a laser beam. From Fig. 5 (i), it can be seen that the boundary
between the plating layer and the substrate is located in the neigh-
borhood of 100 pulses. At the boundary, a concentration of Al caused
by the formation of Fe-Al alloy is observed. The depth profile of
each element at the individual analysis points can be obtained in
about 60 seconds and hence, each sample can be analyzed in 120
seconds.

The results of depth profiling of the normal and defective parts
of Sample C are shown in Figs. 6 (i) and (ii). For the purpose of
simplification, the analysis results for Zn and Fe have been omitted.
A comparison between Fig. 6 (i) and (ii) revealed that Al, Mg, and
Ca were conspicuously detected in the defective part, but that there
was no difference in Na intensity between the normal and the defec-
tive parts. Therefore, we judged that the defect in Sample C was
ascribable to slag.

The EPMA results for the defective parts of Samples A and C are
shown in Figs. 7 and 8. Sample A shows segregations of Ca, Mg, Si,
and Na, whereas Sample C shows segregations of Al, Mg, and Ca.

These elements were found to be the same as the elements that were
confirmed to have been concentrated in the parts analyzed by LIBS.

3.2 Center segregation of slab

Fig. 9 shows elemental maps of the sample with center segrega-
tion. A laser beam was irradiated onto the points of intersection of
the grid lines. As mentioned earlier, the interval of laser irradiation
was 1 mm. In the figure, the dark portions showing high signal in-
tensities represent the segregation of an element. It can be seen that
C and S segregated and that Si was slightly concentrated. Although
Al and Ca were also measured, their concentrations were not con-
firmed. Concerning Fe, the matrix, the signal intensities obtained
were almost the same at all measuring points, except that the segre-
gated part showed slightly higher signal intensity. Thus, we were
unable to observe any influence of the structure of the sample or of
the elements coexisting in the sample. Although we did not test this
in the present study, it is considered possible to obtain more detailed
information about the condition of slab segregation by increasing
the number of elements measured (Mn, P, etc.) and/or improving the
2-dimensional resolution by narrowing the diameter of the laser irra-
diation spot.

4. Conclusion

We developed a new technique to rapidly investigate the causes
of defects in steel using LIBS. By comparing the analysis results
between the normal and the defective parts of a sample, it is possible
Fig. 7 EPMA results for sample (A) (× 1 000)

Fig. 8 EPMA results for sample (C) (× 1 000)

Fig. 9 Elemental mapping results of central segregation

to determine whether the defect is ascribable to certain nonmetallic inclusions (alumina, slag, or mold flux) or to residual scale. With our new technique, the cause of a defect of a given sample can be determined within 30 minutes, including the time required for sample preparation. Hence, it permits the taking of speedy and appropriate action in the manufacturing process. We expect that it will help improve the quality and productivity of steel materials.

References
2) JIS G 0553, 1996