Cathodoluminescence analysis of nonmetallic inclusions of nitrides in steel

doi: 10.1002/sia.6539

Cathodoluminescence analysis of nonmetallic inclusions of nitrides in steel (CL analysis of nitride inclusions in steel)

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Abstract

Identification of nitride inclusions such as boron nitride (BN) and aluminum nitride (AlN) is important in the steelmaking industry because BN inclusions deteriorate the creep strength of ferritic heat-resistant steel, and AlN inclusions cause transverse cracking in twin-induced-plasticity steel. The conventional method employed for the analysis of such inclusions in steel combines optical microscopy and electron probe microanalysis, which is the time-consuming. The aim of this study is to investigate the application of cathodoluminescence (CL) analysis (both images and spectra) to the rapid identification of BN and AlN inclusions. Measurement samples were prepared by heating mixtures of 99 mass% Fe and 1 mass% B or Al powders at 1550°C in a nitrogen atmosphere. BN inclusions larger than 5 μm and AlN inclusions 20 μm in size were identified within 1 s on the basis of their luminescence color (blue-violet for BN and blue for AlN) in the CL images. We demonstrated that BN, AlN, and Al_2O_3 inclusions could be identified from their CL spectra without the conventional method of electron probe microanalysis (EPMA). Capturing a CL image can provide a means of rapidly identifying BN and AlN inclusions in steel. We also carried out CL analysis on a sample containing TiN inclusions which can trigger cleavage fracture in low-carbon steels. No luminescence was detected in the CL image, and there were no CL spectral peaks, indicating that it is difficult to apply CL analysis to the identification of TiN inclusions.

Key-words: Cathodoluminescence, Boron nitride, Aluminum nitride, Steel, Inclusion

Introduction#

The analysis of nonmetallic inclusions in steel, such as oxides (e.g., Al_2O_3, SiO_2, $MgAl_2O_4$), sulphides (e.g., MnS, CaS), and nitrides (e.g., AlN, BN, TiN), is an important step in steel production because these inclusions can create serious problems like breakage of steel wires during drawing, hydrogen-induced cracking, fatigue failure, and surface flaws.[1-3] The amount, size distribution, shape, and composition of such nonmetallic inclusions are normally measured during the inclusion analysis. This is because the contribution of nonmetallic inclusions to the abovementioned problems depends on their composition, size, shape, and amount.[4] Inclusion analysis is typically conducted by a method combining optical microscopy and electron probe microanalysis (EPMA).[5] There has recently been a demand for a reduction in inclusion analysis time to improve the productivity of steel because it takes roughly one week to complete the conventional inclusion analysis.[5] Various kinds of measurement techniques are employed for inclusion analysis:[6,7] spark-induced atomic emission spectrometry, laser microprobe mass spectrometry, transmission electron microscopy (TEM), and atom probe field ion microscopy (APFIM). However, these methods cannot simultaneously identify the composition, size, shape, and amount of inclusions. We have recently demonstrated that capturing cathodoluminescence (CL) images enables $MgAl_2O_4$ spinel and Al_2O_3 inclusions in steels to be distinguished more rapidly than by the conventional method.[8-10] CL analysis is obtaining images and spectra based on the phenomenon of light emission from materials as a result of electron bombardment and can simultaneously identify the amount, size distribution, shape, and occasionally, composition of non-metallic inclusions in steel.[11,12]

In the present study, we demonstrate a method for identifying nonmetallic inclusions of nitrides such as boron nitride (BN) and aluminium nitride (AlN), by investigating their CL spectra and images. The detection of these nitrides is important because they degrade various

properties of steels. For example, although the addition of boron to heat-resistant steels significantly enhances their creep strength,[13] BN precipitation prevents the enhancement of creep strength in steels containing nitrogen, such as ferritic heat-resistant steels with a high chromium content, because of the reduction in the amount of boron dissolved in the steel.[14,15] The addition of a small amount of aluminum leads to transverse cracking problems in peritectic C level steels because AlN may precipitate at the austenite grain boundaries.[16,17]

Experimental

We performed CL analysis on model samples prepared by melting iron (Fe) with boron (B) or aluminum (Al) under a nitrogen atmosphere. A mixture of 99 mass% of electrolytic Fe powder (purity: 99.9%, Wako Pure Chemical Industries, Ltd.) and 1 mass% of B (purity: 99%, Wako Pure Chemical Industries, Ltd.) or Al (purity: 99.9%, Nacalai Tesque, Inc.) powder was placed in an alumina (Al_2O_3) crucible. The mixture was heated at 1550°C for 20 min and then cooled to room temperature in a flowing nitrogen atmosphere (flow rate: 200 ml min^{-1}). The surfaces of the samples were polished using 1200 and 2400-grid abrasive paper. After that, the surfaces were finished using a 1-μm diamond paste.

CL analysis of the model samples was conducted using a custom scanning electron microscope-cathodoluminescence (SEM-CL) system. Details of the SEM-CL system have been reported in our previous papers.[8,9] The main points will be summarized in this section. CL images of the samples were captured through a quartz viewport attached to a commercial SEM instrument (Mighty-8DXL, TECHNEX, Tokyo, Japan) using a digital single-lens reflex camera (α7RII, Sony Corp., Tokyo, Japan) equipped with a zoom lens (LZM-06075A, Seimitu Wave Inc., Kyoto, Japan). The sensitivity range of the camera was from 420 to 680 nm. CL spectra of the samples were acquired using an optical spectrometer (QE65Pro, Ocean Optics Inc., Florida, USA) by attaching a flange to introduce an optical fiber into the SEM

chamber and connecting the optical fiber to the optical spectrometer. Elemental analysis of the samples was carried out using a wavelength dispersive X-ray (WDX) detector equipped with a field emission electron probe microanalyzer (FE-EPMA) (JXA-8530F, JEOL Ltd., Tokyo, Japan).

Results and Discussion

BN precipitation in ferritic heat-resistant steels with a high chromium content degrades the creep strength.[14,15] We attempted to detect BN inclusion by a capturing CL image of the sample prepared by heating a mixture of Fe and B powders at 1550°C under a nitrogen atmosphere. A CL image of the sample is shown in Fig. 1a, and the corresponding SEM image is shown in Fig. 1b. The area emitting blue-violet luminescence in Fig. 1a corresponded to the inclusions observed in the SEM image (Fig. 1b). All inclusions were confirmed to be BN by WDX analysis. A BN inclusion, 5 μm in size (marked 1 in Fig. 1b), was successfully detected by capturing a CL image in 500 ms (Fig. 1a). This indicates that CL images can rapidly detect BN inclusions which may deteriorate the fatigue and impact characteristics of steel because BN inclusions larger than 20 μm deteriorate these characteristics.[15] We also collected the CL spectrum of the BN inclusion (marked 2 in Fig. 1b). The measured CL spectrum is shown in Fig. 1c. Peaks were detected at around 350 and 390 nm. The luminescence color for the BN inclusion is due to the peak at 390 nm and the tail towards longer wavelengths, which are located in the violet (380-450 nm) and blue regions (450-495 nm). The two peaks at 350 and 390 nm are consistent with those reported in previous studies and related to B or N vacancies.[18,19] The present results suggest that the SEM-CL system can identify BN inclusions by yielding a CL image and CL spectrum without any additional measurement of the characteristic X-rays of B and N, the conventional method for detecting BN.

AlN precipitation at grain boundaries causes transverse cracking in twin-induced-plasticity (TWIP) steel.[16,17] Thus, the detection of AlN is important for investigating transverse cracking. We performed CL analysis of a sample prepared by heating a mixture of Fe and Al powders at 1550°C in a nitrogen atmosphere. A CL image of the sample is shown in Fig. 2a, and the corresponding SEM image is shown in Fig. 2b. Inclusions emitting blue (inclusion 3) or pink luminescence (inclusion 4) were detected in the CL image. WDX maps of aluminum, nitrogen, and oxygen in these inclusions (Figs. 3c, d, e) show that inclusion 3 contained aluminum, nitrogen, and a small amount of oxygen, while inclusion 4 contained aluminum and oxygen. These results indicate that inclusion 4 could be Al_2O_3, but it is difficult to determine the phase of inclusion 3 from WDX mapping. We measured the CL spectrum of inclusion 3 (see Fig. 3a). Inclusion 3 showed a broad peak at 400 nm and a small sharp peak at 695 nm, which are consistent with the AlN peaks reported in previous studies.[20,21] The luminescence color of the AlN inclusion is due to the broad peak at 400 nm, which originates from donor-acceptor pair transitions involving an unknown shallow donor and an isolated aluminum vacancy.[20,22] The sharp peak at 695 nm was attributed to an antiferromagnetically coupled cluster of chromium (III) ion (Cr^{3+}).[21] The Cr in inclusion 3 came from the Fe powder and/or the Al_2O_3 crucibles because we confirmed that they contained Cr as an impurity by elemental analysis.[9] Thus, Fig. 3a suggests that inclusion 3 is AlN and that AlN can be identified without WDX analysis by detecting the characteristic CL peaks. It can be inferred that the small amount of oxygen present might be dissolved in the AlN. The CL spectrum of inclusion 4 showed broad peaks at around 545 and 740 nm and a sharp peak at 695 nm, as shown in Fig. 3b. All these peaks are in good agreement with those for alumina (Al_2O_3) reported in previous studies,[23-27] suggesting that inclusion 4 is Al_2O_3. The broad peak at around 545 nm is related to oxygen vacancies in Al_2O_3.[23-25] The sharp peak at 695 nm and the broad peak at around 740 nm are attributed to Cr^{3+} and titanium (III)

ions (Ti^{3+}), respectively, substituting octahedrally coordinated Al^{3+}.[25-27] The Ti in inclusion 4 came from the Al_2O_3 crucible, which was confirmed to contain 40 ppm Ti by elemental analysis.[9]. The oxygen in the inclusions may come from the oxygen in the Fe powder, the Al_2O_3 crucible, and/or the residual oxygen in the nitrogen gas used for sample preparation. These results suggest that we can identify AlN inclusions using the SEM-CL system without a WDX detector even if Al_2O_3 inclusions are also present. Moreover, capturing a CL image enables AlN to be identified much more rapidly, as compared with WDX elemental mapping: it takes approximately 1 h to obtain a WDX elemental map, but only 1 s to capture a CL image. In contrast, it is difficult to distinguish BN and AlN inclusions from their luminescence colors in CL images due to their similar luminescence colors. In this case, we have to distinguish them from their CL spectra.

The addition of titanium (Ti) to low-carbon steel can result in fine titanium nitride (TiN) particles, which inhibit austenite grain growth at high temperatures. However, the addition of excess Ti addition produces TiN inclusions several microns in size, which tend to trigger cleavage fracture.[28,29] Thus, we attempted to identify TiN inclusions by performing CL analysis of a sample prepared by the same method as the samples containing BN and AlN. No luminescence in the CL image or peaks in the CL spectrum were detected for TiN inclusions with the size of approximately 20 μm in the sample. Nor could we detect CL peaks for the TiN reagent (purity: 99%, Kojundo Chemical Laboratory Co., Ltd.). These results could be due to the fact that TiN possesses metal-like properties because metals do not show CL. Thus, it is difficult to identify TiN inclusions by CL analysis.

Conclusion

We demonstrated that it is possible to identify nonmetallic nitride inclusions, namely, BN inclusions larger than 5 μm and AlN inclusions 20 μm in size by examining the CL

images, CL spectra, and WDX elemental maps of inclusions in mixtures of 99 mass% Fe and 1 mass% B or Al powders heated at 1550°C in a nitrogen atmosphere. CL images of the BN and AlN inclusions were captured within 1 s, which was more than 1000 times faster than can be achieved using WDX elemental mapping. We also showed that BN, AlN and Al_2O_3 inclusions can be identified from the CL spectra by comparison with previously reported CL spectra for BN, AlN and Al_2O_3. Thus, CL analysis (both images and spectra) can be used to identify BN and AlN inclusions more rapidly than conventional methods such as EPMA. Future work should focus on examining steel products containing BN or AlN inclusions to apply CL analysis to the identification of AlN and BN inclusions in steel. We also attempted to identify TiN inclusions by capturing CL images. However, no luminescence was detected in this case.

Acknowledgements

Financial support for the present study was provided by JSPS KAKENHI [Grant No. 17H03435]. The authors thank Mr. Issei Narita of Tohoku University for helping us perform the WDX analysis.

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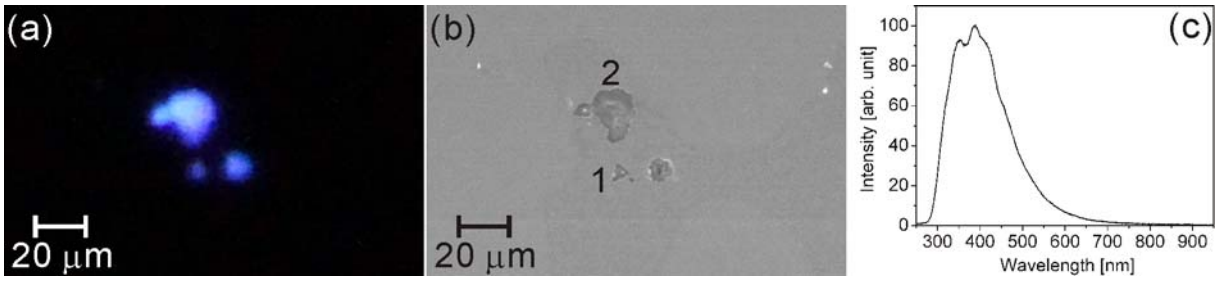

Figure 1. (a) CL and (b) SEM images of polished surface of steel sample prepared by heating mixture of Fe and B powders at 1550°C in a nitrogen atmosphere. The exposure time for the CL image was 0.5 s. (c) CL spectrum of inclusion labeled 2 in Fig. 1b. The measurement duration was 10 s.

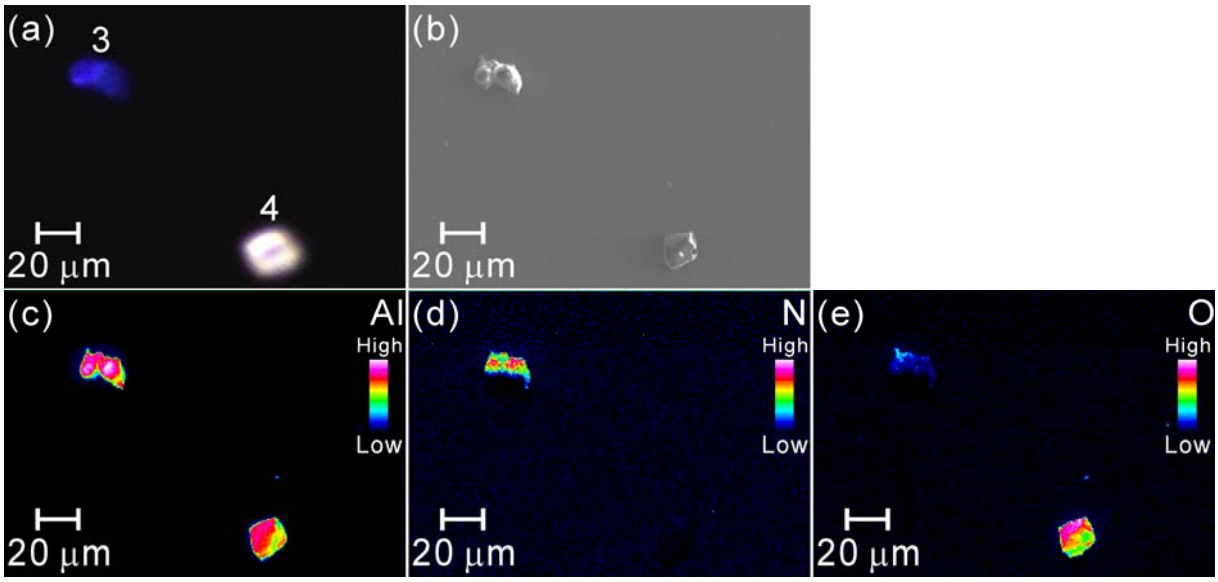

Figure 2. (a) CL image, (b) SEM image, and WDX elemental maps for (c) Al, (d) N, and (e) O for polished surface of steel sample prepared by heating mixture of Fe and Al powders at 1550°C in nitrogen atmosphere.

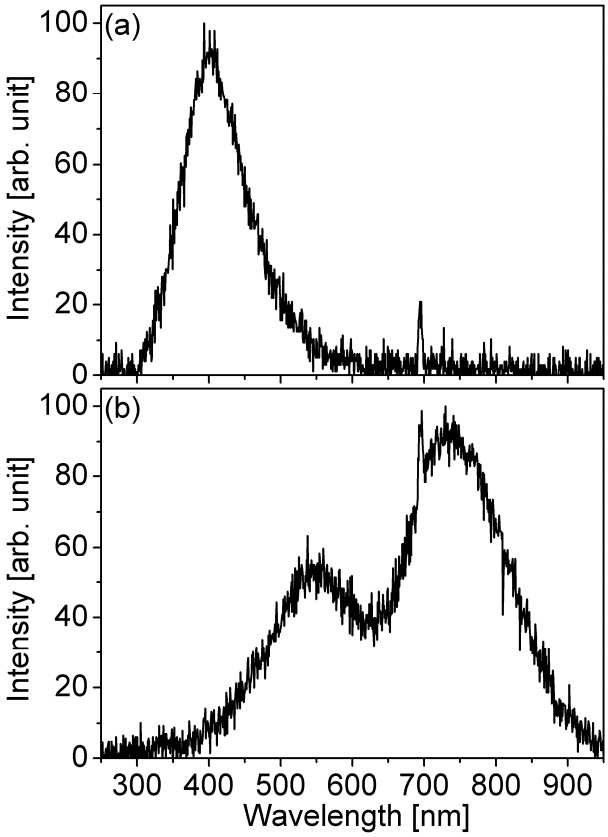

Figure 3. CL spectra of (a) inclusion 3 and (b) inclusion 4 in Fig. 2a. The measurement duration was 100 s.