Paper (Invited)

Low-Voltage Scanning Electron Microscopy as a Tool for Surface Imaging and Analysis of Practical Materials

Masayasu Nagoshi,[1,*,+] Kaoru Sato,[2] and Tomohiro Aoyama[3]
[1] Steel Research Laboratory, JFE Steel Corp., 1-1 Minamiwatarida-cho, Kawasaki 210-0855, Japan.
[2] JFE-Techno Research Corp., 1-1 Minamiwatarida-cho, Kawasaki 210-0855, Japan.
[3] Steel Research Laboratory, JFE Steel Corp., 1 Kokan-cho, Fukuyama 721-8510, Japan.
[*] m-nagoshi@jfe-tec.co.jp

（Received: March 9, 2017; Accepted: June 13, 2017）

Low-voltage scanning electron microscopy (LV-SEM), imaging and energy dispersive x-ray spectroscopy (EDX) analysis, have been applied to steel surfaces in order to clarify the performance of these techniques as a surface analysis. The information depth of LV-SEM imaging is limited by the penetration range of primary electrons. The range also limits the information depth of LV-SEM-EDX analysis. These situations are quite different from those of surface analysis techniques such as Auger electron microscopy in which the escape depth of signal electrons determines the information depth. The information depths of both LV-SEM imaging and LV-SEM-EDX analysis are an order of 10 nm for the primary electron energy of around 1 keV. We can obtain topographic, material, and elemental information from such shallow region of material surfaces with high spatial resolution. This shows that the techniques are applicable to surface analysis of practical materials although the information depth is still deeper by one order than those of the conventional surface analysis techniques.

1. Introduction

Scanning electron microscopy (SEM) is a fundamental technique for material characterizations. SEM has not been categorized, in many cases, to the surface analysis technique such as Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). The main reason is that the information depth of SEM reaches up to a micrometer level when traditional accelerating voltages (5 kV – 30 kV) are adopted. This situation has been changing since low-voltage SEM (LV-SEM [1-3]) instruments having high spatial resolution under low primary electron energy of less than 1 keV were commercially available [4] in this two decades. Jaksch and coworkers demonstrated that such LV-SEM instrument is applicable to high resolution imaging of outermost surface layers and cross sections for several practical materials [5, 6]. We have studied surface imaging and elemental analysis using LV-SEM and applied the techniques to steel surfaces [7 - 9]. Topographic and material information of outermost layers can be obtained simultaneously using different electron detectors under the ultra-low primary energy conditions. It should be emphasized that effective use of wide range primary electron energy, including the ultra-low voltage lower than 1 keV, is important to obtain multiple information of surfaces. Various information, such as crystallographic and atomic-number information, involved in backscattered electron (BSE) images are also extracted by controlling take-off angle and primary electron energy including low values [10, 11]. Elemental analysis for surface layers with the thickness of a few nanometers also become possible when energy dispersive x-ray spectrometer (EDX) is combined with LV-SEM [12]. These results demonstrate that LV-SEM technique has a potential as a surface analysis tool for practical material such as steel.

Recent high-end SEM instrument provides scientists and researchers devoting material surfaces easy operations of high resolution SEM observation with the primary electron energies below 1 keV thanking to novel techniques such as magnetic-electrostatic hybrid lenses and negative stage bias systems. However, there are still few studies in which the advantages of LV-SEM

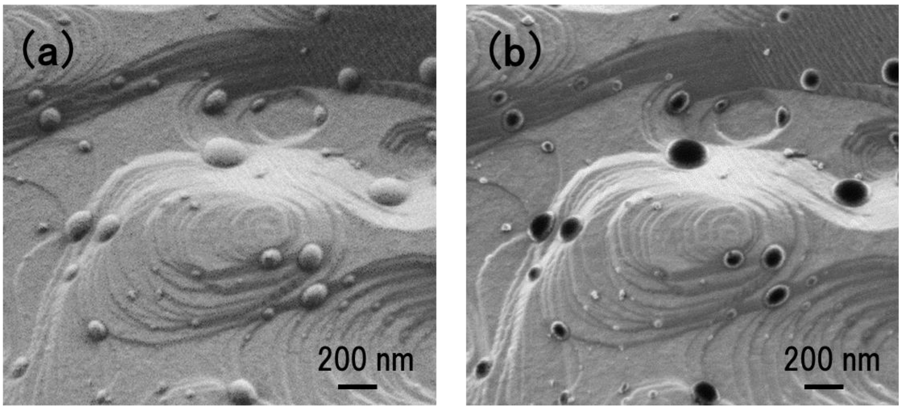

Fig. 1. SEM images obtained for the identical area of a steel surface using an Everhart-Thornley detector (a) and an in-lens detector (b). Primary electron energy was 0.5 keV and working distance was 4 mm. Topographic and material contrasts were extracted using the different detectors.

techniques were fully utilized in the field of fundamental sciences and practical analysis for material surfaces. In many studies the instruments have been used under traditional experimental conditions namely the primary electron energy ranging from 5 keV to 20 keV. This situation was clear when we saw poster presentations in the 7th Internal Symposium on Practical Surface Analysis (PSA-16) held in Daejeon, Korea in 2016 [13]. SEM images were presented in 14 posters and a half of the images were obtained using ordinal primary electron energy of 5 keV and over. Primary electron energy was not documented, surprisingly, for the remaining image data.

In this paper we present our recent LV-SEM images and LV-SEM-EDX results obtained for steel surfaces. Advantages, limitations, and prospects of LV-SEM techniques are discussed in the viewpoint of the practical surface analysis.

2. Experimental

Field emission SEM (FE-SEM) instruments having a GEMINI column were used in this study. The column is characterized by a combination of a beam booster, a magnetic/electrostatic objective lens, and in-lens detector(s). These unique components contribute to the high resolution imaging with low primary electron energy [4]. Weak stray magnetic field on the specimen surface is advantageous for observation of steel material having ferromagnetisms. We have used models LEO1530 and SUPRA 55 VP (now Carl Zeiss Microscopy, Germany). These instruments have an annular type in-lens (IL) detector and a traditional Everhart-Thornley (ET) detector. Primary electron energies lower than 1 keV were used for imaging and those from 1.5 keV to 10 keV were used for EDX analysis. A conventional solid state detector (SSD, Vantage, Thermo Noran, USA) was used for EDX analysis. We also used a newly developed window-less silicon drift detector (SDD, X-MAX/Extreme, Oxford instrument, UK) equipped with a model Merlin (Carl Zeiss Microscopy) in cooperation with Oxford instrument.

Surface of a cold rolled steel sheet was observed without any surface treatment except for degreasing using organic solvents. Oxide particles mainly consisting of boron and manganese precipitate on the surface. There are small step-like structures on the steel matrix surface. The oxides and structures are formed during an annealing process. These components are suitable for evaluating material contrast and topographic contrasts in LV-SEM images.

3. Results and discussion

3.1 Imaging steel surfaces by LV-SEM

Figure 1 shows SEM images obtained by an ET detector (a) and an IL detector (b) for the identical area of a steel surface. A model LEO1530 was used and the primary electron energy was set to 0.5 keV. Topographic contrast dominates in the ET detector image in Fig. 1(a). Surface oxide particles are highlighted by their dark contrast (positive charging contrast) in Fig. 1(b), which is superimposed to the topographic contrast. These differences were explained by the difference in kinetic energy ranges of detected secondary electrons between two detectors [7 – 9]. An electrostatic field of the objective lens accelerates emitted electrons and introduces them into the column. Almost all the emitted electrons with lower kinetic energy are sucked in the column by the field [14]. As a result, the IL detector mainly detects electrons emitted with low kinetic energy and the ET detector detects remaining electrons with higher kinetic energy. Positive charging reduces yield of emitted electrons with the kinetic energy of less than a few electron-volts [2], the material contrast due to the positive charging appears only in the IL detector image as shown in Fig.1 (b). After understanding such information-selection mechanisms, namely selective detections of emitted electrons, we can extract specific information by controlling observation parameters such as working distance (WD) [15] and energy filtering [16]. The selective electron detections are now available to other SEM instruments [17].

Penetration range of primary electrons should be shorter than the thickness of oxide particles in order to keep positive charging shown in Fig. 1(b). The information depth of the material contrast is then evaluated by the maximum penetration range of primary electrons. One can estimate the penetration range roughly by a simple equation [18] or Monte-Calro simulation. In the case of SiO_2 films on Si the information depth was estimated to be about 10 nm for the primary electrons with the kinetic energy of 0.4 keV [19]. The range was estimated to be about 15 nm for Cr with the primary electron energy of 1.5 keV (see Fig.3. We estimated the value as the maximum depth of the primary electron penetration profile derived by a Monte-Carlo simulation.). Information depth of ET detector image (Fig.1 (a)) might be shorter than that of the material contrast because the detector does not detect low-kinetic-energy electrons having long inelastic mean free path (IMFP). Careful experiments and theoretical examinations are needed to discuss this issue.

There is no fundamental limit of primary electron energy for SEM imaging. The minimum values of IMFP locate around 50 eV [20]. Very low primary electron energy has been achieved by a negative specimen bias technique; scanning low energy electron microscopy (SLEEM) [21]. A pioneering work showed that the technique is applicable to investigation of practical material surfaces [22]. This technique is more surface sensitive and applicable for imaging of steel surfaces using recent SEM instruments [23].

3.2 Elemental analysis using LV-SEM-EDX

The information depth of SEM-EDX analysis reaches to a micrometer level when we use usual primary electron energy ranging from 10 keV to 20 keV. This depth range is more than 100 times deeper than the information depth of the LV-SEM imaging mentioned in the previous section. A big mismatch of the information depth between imaging and elemental analysis potentially lead researchers to misunderstandings of the material surface structures. EDX analysis under the LV conditions is a crucial approach to avoid the risks. EDX spectra were recorded with the primary electron energy of 1.5 keV – 15 keV for Cr films with the thickness of 2 nm and 20 nm on Fe [12]. Figure 2 shows the spectra measured with the primary electron energy of 1.5 keV (a) and 5 keV (b). Fe-L emission peak exists on the spectrum recorded for 2 nm – Cr film but disappears on that for 20 nm when the primary electron energy was set to 1.5 keV (Fig. 2(a)). These results show that the information depth of Fe-L X-ray is a value between 2 nm and 20 nm for the primary electron with the energy of 1.5 keV. Figure 3 shows penetration profiles of the primary electron (kinetic energy is 1.5, 5, and 10 keV) and depth distributions of Cr-L X-ray emission for metallic Cr matrix estimated by a Monte-Carlo simulation (Flight Simulator). Incoming angle of the primary electron and take-off angle of X-ray emission were set to 0 and 60 degrees to the surface normal, respectively. The detection depth of Cr-L line in chromium layer was estimated to be about 10 nm for the primary electron energy of 1.5 keV. This value is in good agreement with the experimental results (between 2 and 20 nm) although energy of emis-

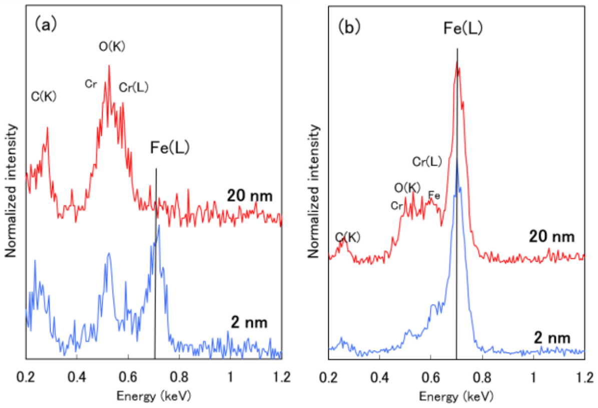

Fig. 2. (color online) EDX spectra measured for Cr films on Fe with the thickness of 2 nm and 20 nm. The primary electron energy was set to 1.5 keV (a) and 5 keV (b). Spectra measured at 1.5 keV show a higher surface sensitivity.

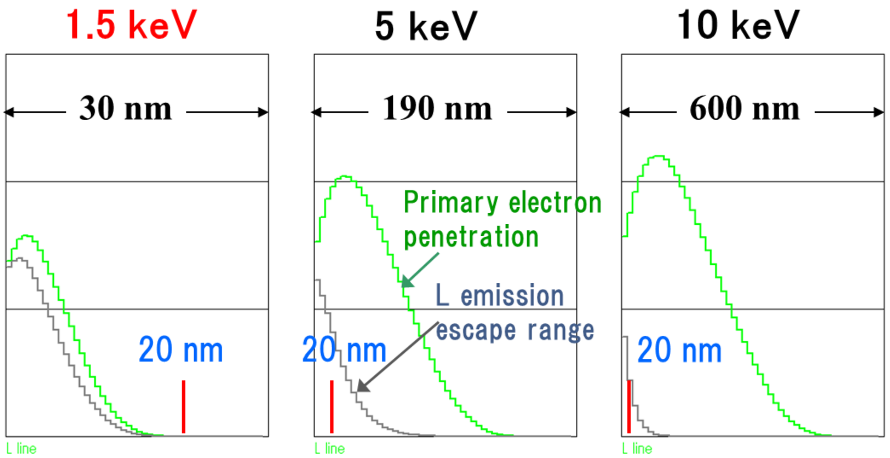

Fig. 3. (color online) Monte-Carlo simulation results of depth distributions of primary electron penetration and Cr-L emission for Cr matrix. The primary electron energy was set to 1.5, 5, and 10 keV and is denoted in the figure. Incident and escape angles were set to zero and 60 degrees to the surface normal, respectively. The information depth is limited by the primary electron penetration at 1.5 keV. On the contrary, that is limited by the escape depth of Cr-L X-ray at 5 and 10 keV.

sion lines are different (Cr-L and Fe-L line). We should note that the penetration range of primary electron limits the information depth of SEM-EDX analysis for the primary electron energy of 1.5 keV. On the contrary, the escape depth of X-ray limits the information depth for conventional primary electron energy; 5 keV and 10 keV. The situation for LV-SEM-EDX is also different from that for surface analysis techniques such AES in which the escape depth of signal electrons determine the information depth.

We can obtain topographic, material and elemental information from almost the same depth range of a ten nanometer order when SEM observation and EDX analysis are carried out using the identical ultra-low primary electron energy. This is because that both information depths are limited by the penetration range of low-energy primary electrons, which is clearly shown in Fig. 3 (the energy is 1.5 keV).

Figure 4 shows SEM images and EDX apparent concentration maps calculated using B-K, O-K, Mn-L, and Fe-L lines recorded for the identical area of a steel surface with the primary electron energies of 1.5 keV (upper panels) and 10 keV (lower panels). In this experiment, an in-lens back scattered electron (BSE) detector was used to obtain material information. BSE images highlight the distribution of surface particles and EDX concentration maps clearly show that the particles consist of B, O and Mn (upper panels). It is impossible to realize the latter characteristics if a conventional primary electron energy, 10 kV, is used for EDX analysis as shown in the lower panel of Fig.4. B-K concentration map shows no contrast and Mn-L concentration map shows a distinct distribution. The spatial resolution of the O-K concentration map significantly improves as the primary electron energy decreases from 10 keV to 1.5 keV. The reduction of penetration range toward the horizontal direction of the material surface provides high spatial resolution of not only surface imaging but also elemental analysis. The SEM images and X-ray concentration maps in Fig.4 were recorded with the identical WD of about 4 mm. This is important because an optimum WD is around 4 mm in this type of SEM instrument for obtaining material and topographic information simultaneously [15]. The WD of 4 mm is too short for conventional EDX systems due to geometrical limitations. A new EDX instrument (X-Max Extreme, Oxford Instruments) used in this study has solved the problem due to its novel design [24].

The information depth of LV-SEM-EDX shown in this study is still 10 times deeper than that of AES and XPS. The information depth of about 10 nm is a limit when conventional LV-SEM and EDX instruments are used. One reason is that number of detected elements is seriously limited when common X-ray emission lines are used. Transition edge sensor (TES) spectrometer [25], soft X-ray emission spectrometer (SXES) [26], and window-less EDX spectrometer [24] have a potential to detect X-ray emission with lower energy. This provides us a possibility of using lower primary electron energy for

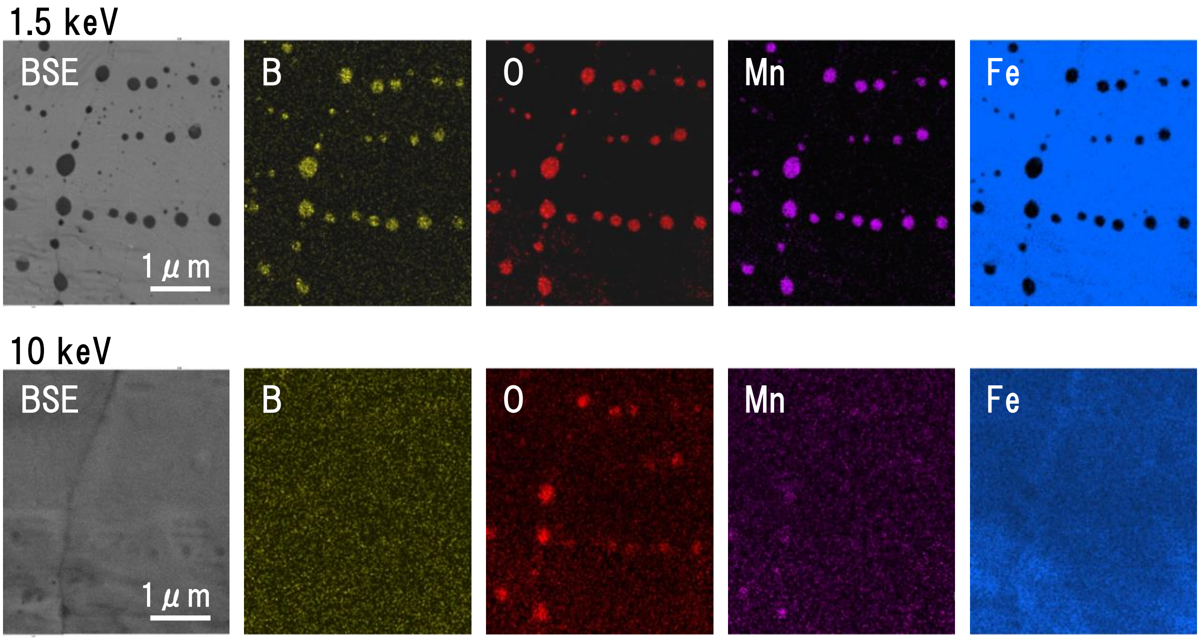

Fig. 4. (color online) BSE images and EDX concentration maps calculated using B-K, O-K, Mn-L, and Fe-L X-ray emissions for the identical area of a steel surface. Primary electron energy was set to 1.5 keV (upper panel) and 10 keV (lower panel). Comparison between two data sets clearly shows significantly high surface sensitivity and spatial resolution of the analysis with the primary electrons energy of 1.5 keV.

elemental analysis. The key point is sensitivity of the detection because cross sections of electron-induced X-ray emission decrease with decreasing of the primary electron energy.

TES spectrometer and SXES provide higher X-ray energy resolutions than ordinal SSD and SDD. Especially, SXES having diffraction grating devices has showed the energy resolution better than 0.3 eV for the Fermi edge of metallic Al [26]. The higher energy resolutions are advantageous for detecting X-ray peaks in the very low energy X-ray region where many emission lines exist. High energy resolution also makes it possible to investigate chemical states of elements. Metallic and oxidized states of Fe were distinguished from the Fe-L emission spectra measured by a TES spectrometer [27]. A database of SXES spectra has been favorably developed for reference materials [28]. These characteristics of new spectrometers can provide us a chance to investigate chemical states of element at small areas of material surfaces by the combination with the LV-SEM technique.

Quantitative elemental analysis using LV-SEM-EDX is still under development. Atomic ratios of Fe and Ni were satisfactorily estimated for a model Fe-Ni alloy set using L emission lines of Fe and Ni [12]. The quantitativity for more complex practical materials especially containing light elements should be studied. Further experimental and theoretical approaches are needed to establish quantitative analysis techniques of LV-SEM-EDX. Higher surface sensitivity of LV-SEM and LV-SEM-EDX means that imaging and analysis are easily affected by contaminations or degradations of top most surfaces. This is obviously seen in Fig.2 in which relative intensities of C-K and O-K lines are notably higher in the spectra measured with the primary electron energy of 1.5 keV (a) than those of 5 keV (b). These effects may sometimes smear out structural and elemental information of real material surfaces although the effects are less serious than that in the surface analysis techniques. Anti-contamination techniques and surface treatments are important for some applications of LV-SEM and LV-SEM-EDX.

4. Conclusion

We have demonstrated that LV-SEM and LV-SEM-EDX have a potential of opening a new window in the field of surface analysis for practical materials. The information depths of both imaging and analysis are limited by the penetration range of primary electrons and estimated to be about 10 nm under the experimental conditions used in this study. This information depth is remarkably shallower than that of conventional SEM imaging and SEM-EDX analysis although the information depth of analysis is still deeper than those of surface analysis techniques such as AES. SLEEM technique and newly developed X-Ray spectrometers have potentials to reduce the information depth of imaging and elemental analysis, respectively. Higher surface sensitivity of the techniques requires further research works to improve quantitative ability and reduce contamination effects. Continuous experimental and theoretical investigations are needed for the progresses of the techniques.

5. Acknowledgements

The authors never forget the late Dr. H. Jaksch and the late Prof. J. Cazaux. They gave us valuable comments on our work and warm encouragements. We thank Dr. Simon Burgess and Oxford Instruments plc for fruitful collaboration about their newly developed window-less SDD. Our thanks also go to researchers and engineers outside and inside of JFE Steel Corporation for fruitful collaborations.

6. References

+ Present Address: JFE-Techno Research Corp., 1-1 Minamiwatarida-cho, Kawasaki 210-0855, Japan.

[1] J. Pawley, *J. Microsc.*, **136**, 45 (1984).

[2] L. Reimer, in “Image Formation in Low-Voltage Scanning Electron Microscopy”, SPIE, Washington, (1993).

[3] L. Reimer, Scanning Electron Microscopy. 2nd ed. Springer-Verlag, Berlin, Heidelberg, (1998).

[4] J.-P. Martin, V. Drexel, H. Jaksch, and E. Weimer, *Zeiss Information with Jena Review*, **4**, [5], 14 (1995).

[5] H. Jaksch and J. P. Martin, *Fresenius J. Anal. Chem.*, **353**, 378 (1995).

[6] D. Pohl and H. Jacksh, in Advances in Scanning Electron Microscopy, Prakt. Metallogr., **33**, 235 (1996).

[7] M. Nagoshi, T. Kawano, and K. Sato, *J. Surf. Finish. Soc. Jpn.*, **54**, 35 (2003).

[8] K. Sato, M. Nagoshi, T. Kawano, and Y. Homma, *OYOBUTURI (Applied Physics)* **73**, 325 (2004).

[9] M. Nagoshi, T. Kawano, and K. Sato, Proc. Asia Steel International Conference 2006 (Asia Steel' 06), ISIJ, 836 (2006).

[10] T. Aoyama, M. Nagoshi, H. Nagano, K. Sato, and S. Tachibana, *ISIJ Int.,* **51**, 1487 (2011).

[11] T. Aoyama, M. Nagoshi, and K. Sato, *Microscopy*, **64**, 319 (2015).

[12] M.Nagoshi and K.Sato, *Surf. Interface Anal.*, **46**, 865 (2014).

[13] Abstract of 7th International Symposium on Practical Surface Analysis (PSA-16), October 16-21, 2016, Daejeon, South Korea.

[14] K. Kumagai and T. Sekiguchi, *Ultramicroscopy*, **109**, 368 (2009).

[15] M. Nagoshi, T. Kawano, and K. Sato, *Surf. Interface Anal.*, **48**, 470 (2016).

[16] M. Nagoshi, T. Aoyama, and K. Sato, *Ultramicroscopy*, **120**, 20 (2013).

[17] S. Mikmekova, H. Nakamichi, and M. Nagoshi, Abstract of The 16th European Microscopy Congress 2016 (2016). DOI: 10.1002/9783527808465.EMC2016.5865

[18] C. D. Wagner, L. E. Davis, and W. M. Riggs, *Surf. Interface Anal.*, **2**, 53 (1980).

[19] M. Nagoshi, T. Kawano, and K. Sato, *e-J. Surf. Sci. Nanotech.* **6**, 35 (2008).

[20] S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.*, **21**, 165 (1994).

[21] I. Mullerova and L. Frank, *Scanning*, **15**, 193 (1993).

[22] L. Frank, I.Mullerova, K.Matsuda, and S. Ikeno, Materials Transactions 48, 944 (2007).

[23] S. Mikmekova, H. Noro, and K. Yamada, *Microscopy* **62**, 589 (2013).

[24] J. Sagar, S. Burgess, J.Holland, X. Li, and F. Bauer, *Microscopy Today* **25**, 20 (2017).

[25] K. Tanaka, A. Nagata, N. Sasayama, M. Ikeda, A.Odawara, S. Nakayama, and K. Chinone, *J. Surf. Anal.*, **12**, 122 (2005).

[26] H. Takahashi et al., *JEOL news* (Japanese) **44**, 55 (2012).

[27] H. Noro, K. Sato, and K.Tanaka, *Hyomen Kagaku (Surf. Sci. Soc. Jpn.)* **31**, 610 (2010).

[28] M.Terauchi, H.Takahashi, M.Takakura, and T.Murano, “Handbook of Soft X-ray Emission Spectra”, Version 3.0 (Jul. 2016), JEOL Ltd.

Discussions and Q&A with Reviewers

Reviewer #1 Mineharu Suzuki (NIMS)

This paper introduces interesting advantages of LV-SEM as well as LV-EDX to apply the practical surface analysis of the steel material. I strongly recommend the editor to accept it as a JSA article after small revisions to be more informative.

[Q1_1]

In the last part of Experimental chapter, the authors say the specimen was processed by heat treatment. It may be needed to describe the temperature (e.g. 500 K) and environment (e.g. in nitrogen gas).

[A1_1]

We express our thanks to you for your careful review and useful scientific comments which have improved our paper.

We have no precise information about the temperature and atmosphere when the specimen was annealed because the specimen is a piece cut from a commercial cold rolled steel sheet. The annealing condition (N-H_2 environment in many cases) is usually a reduction atmosphere for iron but is an oxidation one for some elements such as silicon and manganese. Therefore the latter elements (B and Mn in this case) segregate on the steel surface as oxides as shown in Figs. 1 and 4. We gave small changes to explain that both oxides and step-like structure were formed during an annealing process.

[Q1_2]

Figure 1 shows the very interesting images using ET and IL. I recommend describing the information on the angle of incidence of the primary electron beam and the angle of detection from the averaged specimen surface for ET and IL, respectively. Can authors discuss on effects of these angles and estimate the minimum step height?

[A1_2]

The angle of incidence of primary electron beam is normal to the specimen surface. It is not easy to know the detection angles for each detector (take-off angles of electrons detected by each detector, to be exact) because trajectory of the emitted electrons is strongly affected by electric and magnetic fields in the SEM instrument. The take-off angle of detected electrons, however, is one of the most important factors to understand contrasts in LV-SEM images. We have tried to understand this by an electron trajectory calculation [K.Tandokoro, M.Nagoshi, K.Sato, K.Tsuno, CAMP-ISIJ* 172, 870 (2016).]. We have no idea to estimate the step height form our SEM images at this moment.

> * *Current Advances in Materials and Processes: report of the Iron and Steel Institute of Japan meeting*.

Reviewer #2 (private)

This paper presents the latest application of LV-SEM for surface analysis, introducing the up-to-date techniques and devices. The authors carefully discuss the information depth of LV-SEM-EDX comparing to that of conventional SEM-EDX. This article should be informative not only to the SEM users but also to the readers of JSA who works on the other surface analysis.