Development of soft X-ray emission spectrometer for EPMA/SEM and its application

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Abstract. A newly developed wavelength-dispersive soft X-ray emission spectrometer (WD-SXES) with two kinds of gratings, JS50XL and JS200N, were installed on electron probe microanalysers (EPMA) and scanning electron microscopes (SEM). The new detector covers the energy range from 50 to 210 eV with an energy resolution of better than 0.2 eV at Al-L emission on Al metal. With this low energy range and high energy resolution, various kinds of X-ray lines of K, L, M, N emission spectra from lithium to uranium could be observed and chemical state analysis carried out. This WD-SXES has also a high potential for analysing trace light elements under 100 ppm. The design, having no mechanically scanning components, allows parallel spectral acquisition over the entire energy range of each grating (50 to 170 eV and 70 to 210 eV).

1. Introduction

Due to the ongoing evolution of the hardware and, later, the software [1] of EPMA/SEM since their development over half century ago, these instruments have continued to be applied to not only scientific but also industrial fields. According to the development and association of various detectors and analysers, instrument capabilities have been expanded to observe and analyze into the microscale and even the nanoscale. The drive for further improvements are continuing for many kinds of fields. On the other hand, the history of transmission electron microscope (TEM) is longer and it provides invaluable capabilities for the characterisation and understanding new materials by techniques such as high resolution observation up to atomic resolution, combined with elemental analysis by SDD (silicon drift detector), crystalline information by electron diffraction and chemical state analysis by electron energy loss spectrometer (EELS). However, sample preparation for TEM is often time intensive compared to that of EPMA/SEM.

Up until now, a conventional method of chemical state analysis with EPMA/SEM has largely been lacking. Our newly developed wavelength-dispersive soft X-ray emission spectrometer (WD-SXES, JEOL SS-94000 SXES) for EPMA/SEM has a high energy resolution of 0.2 eV for Al-L emission spectrum of Al metal [2-4]. This resolution is competitive to that of EELS and XPS. This capability of chemical state analysis realizes the full characterisation of bulk samples with EPMA/SEM using three techniques: elemental analysis by EDS/WDS, crystalline analysis by EBSD and chemical state
analysis by WD-SXES. In this report, the principle and the development of the new WD-SXES spectrometer is presented. Application examples for practical samples and their several functions are also demonstrated. The applicable EPMA and SEM are as follows: EPMA; JXA-8500F, -8100, -8200, 8530F, -8230, SEM; JSM-7100F, -7800F, -7800FPrime, -7200F.

2. Principle
The diffraction grating has been well used as a device of soft X-ray spectroscopy for many years. However, due to the poor sensitivity and narrow X-ray wavelength (energy) region of spectrometers, this method was not widely employed. Due to the recent innovations of very sensitive back-illuminated CCD cameras and a varied line spacing grating, in which the pattern of line spacing is designed to optimize X-ray detection, a new spectrometer has been developed. In this new spectrometer, the project designed the specification which covered the energy range from 50 to 170 eV. It is possible to detect Li-K emission, and the energy resolution is at least 0.3 eV at Al-L emission on Al metal. Moreover, this analysis system provides parallel detection of X-rays over its whole energy range. For the purpose of detection from 50 to 170 eV with high energy resolution, the new type of grating is named JS50XL. For the requirement for more trace element analysis for B, C, and N, a 2nd grating, JS200N, was developed, which covers the energy range from 70 to 210 eV. The spectrometer can have both kinds of gratings installed and can be alternated by a simple switch. When the gratings are switched, the position reproducibility is very high, resulting in no requirement for recalibration.

2.1. Spectroscopic principle due to varied line spacing grating
In order to take parallel detection for several X-rays at the same time, this system does not apply the Rowland circle geometry but uses the fixed grating with varied line spacing (5). The groove is 1,200 lines per mm at the centre of grating. Intermediate between the grating and sample, the focal mirror was applied. It is flexible to adjust the optimum focal condition, comparable to poly-capillary optics. The reproducibility of spectra is expected to be under 1 or 2 pixels difference. It has extremely good performance which is capable of providing chemical state spectra. The spectroscopic principle of the laminar type varied line spacing grating is described as shown in eq. 1 and figure 1 in which the incident angle is constant and the exit angle is dependent on the wavelength of the X-rays. In this laminar type grating, the high order X-ray intensity is smaller than that of brazed type of grating. Normally it is preferred to avoid interference with higher order X-rays. However, these higher order reflections are useful to allow the detection of higher energy X-rays within the energy ranges of the gratings: Using 1st order X-rays, the detection energy range is from 50 to 210 eV but, using higher order X-rays, this is extended in practice up to approximately 700 eV.

\[ d(\sin\alpha + \sin\beta) = m\lambda \]

where \(d\) = width, \(\alpha\) = incident angle, \(\beta\) = exit angle, \(\lambda\) = wavelength, and \(m\) = order of diffraction.

![Figure 1. Schematic illustration of X-ray diffraction from a grating surface.](image)
In conventional WDS, the X-rays are dispersed by Bragg’s law using a Rowland circle geometry of X-ray source, analysing crystals and detector. In this new design, the focal plane is flat field at the CCD device using the varied line spacing grating. This grating pattern, which is produced by a holographic exposure method [7], was optimized for high energy resolution and small scatter. The grating is slightly concave with correction for aberration and greater groove spacing closer to the X-ray generation point. As shown in figure 2, X-rays with the same energy but emitted in different directions are diffracted by the grating to the same height on the CCD detector, and exhibited as a spectrum in the PC system. This is very similar to the EELS system.

![Figure 2. Illustration of parallel detection method of different energy X-rays.](image)

The geometry of this spectrometer is shown in figure 3. In case of JS50XL, the incident angle, $\alpha$, is 86° and emergent angle, $\beta$, is 87°. The size of grating is 50 x 30 mm. From these parameters, the solid angles are approximately estimated to be 0.017 mstr (JS200N) and 0.024 mstr (JS50XL), respectively.

2.2. Back-illuminated CCD

In order to detect low energy X-rays (soft X-rays), a very sensitive non-coated back-illuminated CCD camera has been utilized. The camera is a full-frame back-illuminated CCD camera, 2048 x 2048 pixels, pixel size 13.5 x 13.5 µm, dynamic range of electric charge; 80,000 electrons. The soft X-rays are detected at the Si base plate at the front side of the CCD device without X-ray absorption. This type of CCD is superior for low noise and good sensitivity in detecting low energy X-rays from 10 eV to approximately 1,000 eV than that of a conventional CCD.

3. Feature

According to the specification of the spectrometer, soft X-rays from 50 eV to 210 eV can be detected with a high energy resolution. From the X-ray diffraction eq. 1, higher order X-rays can also be detected. From practical experimental results, X-rays up to approximately 700 eV can be detected.

3.1. What kinds of X-rays

In this low energy range, the possibility of detection for soft X-rays using conventional WDS or EDS is very poor. However, the developed SXES can provide a range of possibilities for these kinds of soft X-ray lines. As these X-ray lines are unfamiliar for microanalysis users, the Bearden’s wavelength table is useful to give an overview and to consider the different types of soft X-ray lines that could be detected [8]. From this table, the relationship between atomic number and various X-ray energies were plotted and shown in figure 4. The region from 50 eV to 210 eV is coloured light grey and that from 210 to 700 eV is coloured dark grey. From this figure, it is understood that SXES that it is
possible to analyse almost every element from lithium to uranium, with the exception of only a few elements.

**Figure 3.** X-ray path of SXES and varied line spacing grating JS50XL.

**Figure 4.** Plotted graph from table 5 in Ref. [5].
3.1.1. K emission spectra. Observable 1st order K emission spectra of SXES are Li, Be and B. Using the higher order K emission spectra, C, N, O and F can be observed. With the high energy resolution of these spectra, better than that of WDS, chemical bonding state analysis is achievable. In figure 5, the difference between Li-K emission spectra obtained from metallic lithium and lithium fluoride can be seen. In the case of lithium metal, without corrosion by exposure to air, Li-K emission is easily observed [9]. In the case of LiF sample, using a soft beam condition, it is difficult to detect Li-K emission. However, if the electron beam is increased, F-K emission can be recorded.

![Figure 5. Li-K spectra of metallic lithium (left) and lithium fluoride (right).](image)

3.1.2. L emission spectra (1): L_{2,3}M_{1} (Mg, Al, Si, P, Cl). Using a standard specification, Al-L emission spectrum can be detected. By adjusting the lower limit to less than 50 eV, Mg-L emission spectrum can be also detected. However, if the spectrometer is adjusted in an attempt to achieve less than 45 eV, the spectrometer’s condition would be out of the ideal diffraction condition and the energy resolution would be dramatically reduced. For metallic Mg and Al, the peak profile corresponding to the Fermi-edge can be observed very sharply like a steep wall, as shown in figure 6. Using this sharpness, the energy resolution of this spectrometer can be evaluated. Since the resolution of the spectrometer is better than the natural width of the X-ray line, a full width half maximum (FWHM) specification, like the EDS resolution method, is unsuitable. The energy resolution of SXES is specified as the energy width between 75 % and 25 % of the distance from top to background of the Fermi-edge. This definition takes into account the broadening of the Fermi-edge due to finite temperature. From this determination method, a resolution of 0.3 eV is guaranteed whilst in practice 0.2 eV is attainable.

![Figure 6. Mg-L and Al-L spectra for pure element.](image)
This sharply defined Al-L Fermi-edge is always observed, on both Al-compounds and Al metals. The lower profile form of the Fermi-edge corresponds to the energy density of state. In other words, as described in Fabian’s textbook, this profile corresponds to the 1st to 4th Brillouin zone [10]. A similar examination can be performed on Si-compounds and P-compounds under the same conditions. In the case of a Si-wafer, a sharp Fermi-edge is not observed since it is modified by sp3 combination band structures.

3.1.3 L emission spectra (2): Lℓ; L3-M1 (Ti, V, Cr, Mn). In the case of the transition elements such as Ti, V, Cr, and Mn, the Lℓ X-ray line has a higher intensity than that of the Lα and Lβ. Lℓ is produced by an L3-M1 transition whilst Lα and Lβ are from L3-M5 and L2-M4 transitions. The Lℓ is a higher energy than Lα and Lβ, and also has a lower absorption problem than that of the absorption edge between Lα and Lβ. For these reasons, Lℓ is expected to provide chemical state information and allow for quantification by low voltage analysis. Lℓ-spectra of Ti-compounds are shown in figure 7. In the case of Ti-oxides, peak shift and sub shoulder peak shapes are observed in correspondence with valence bonds. For Ti4+, such as SrTiO3, the peak shift and peak shoulder at the higher energy side is smaller than for Ti-metal (ground state). These practical spectra will be considered in comparison with chemical calculations and discussed in a future study. From the understanding of the Ti-spectra, the low voltage analysis of the V- and Cr-spectra can then be applied in a similar manner.

3.1.4 M emission spectra. For the 5th period elements of Zr, Nb, Mo, Ag, Cd, Sn, and Sb, the Mz-line of the spectra gives the strongest and sharpest peak. The peak profiles of Zr-Mz and Nb-Mz are shown in figure 8. For Zr and Mo, experiment condition was 5 kV, 100 nA, 5 min JS200N, and for Nb, was 5 kV, 50 nA, 5 min JS200N. The peak height for higher order X-rays for elements with a higher atomic number reduces to a greater degree than Lℓ of the lighter transition metals. As with the Lℓ peak, a similar low voltage analysis capability of the Mz is expected.

3.1.5 N-band emission spectra. Each spectrum of the three elements Pt, Au and Bi in the sixth row of periodic table of the elements shows a distinct peak consisting of a few sub-peaks in the energy range between 120 eV and 150 eV, as shown in figure 9. As far as the present authors are aware, these peaks have not been reported in any literature to date and do not appear in any known data tables. They are tentatively assigned to the second order emission from N-bands. The shapes of the Pt and Au peaks look rather similar. In fact, if the sub-peak at 140 eV is ignored, the peaks consist of two main sub-peaks, the position of which shifts to the higher energy by about 50 eV with the increasing of the atomic number from Pt to Au. The similar systematic energy shift of the two main sub-peaks

![Figure 7. Comparison of Ti-Lℓ spectra for Ti-compounds](Courtesy of CSIRO, Colin MacRae and Nick Wilson).
has been observed in spectra of a series of the sixth row elements; starting from Hf, continuing to Ta, W, Re, Os, Ir, Pt until Au. Although the shapes of the peaks of Pt and Au are similar, slight difference can be noticed. The Bi-peak shape was observed to be different to that from the other sixth row elements. Many features in these series of spectra, including the peaks described above, will also be studied in greater detail in a further study.

4. Application

4.1. Chemical state spectral mapping of a lithium ion battery

Recently the spectral mapping of chemical state by WD-SXES has been developed and applied to various kinds of materials. For example, three samples A, B and C of a lithium-ion battery anode with different charging conditions: 0 % (A), 30 % (B), and 100 % (C), were supplied separately sealed in three glove bags filled with Ar gas. They were transferred to a sample holder in a glove-bag type of wrapper filled with Ar gas, which covered both the sample holder and the insertion chamber of the EPMA as shown in figure 10a. Though cumbersome, this precaution was necessary to avoid chemical reactions of the sample surface in atmospheric air. The three samples, each of which had a length of 50 mm and a width of 30 mm, were mounted on the sample holder side by side as shown in figure 10b. A large area, 30 x 80 mm, was selected for spectral mapping of the chemical state of the lithium. The mapping area consisted of: A and B, with a part length of 30 mm and the full width of 30 mm, and C,
with a part length of 30 mm and a part width of 20 mm. This area was divided into 30 x 50 pixels so that the inter-pixel distance was 1.0 mm in the length direction and 1.6 mm in the width direction. Using a diameter of 1 µm and a beam current of 0.8 µA at an accelerating voltage of 2 kV the intensities of X-rays in the energy range between 48 and 165 eV were acquired for 60 s/pixel. Three maps were constructed by using the X-rays in three energy ranges corresponding to sub peak of Li-K (49 - 51 eV), Li-K (53 - 55.5 eV) and C-K of the 3rd order (nominally 93 - 96 eV) and are shown in figure 11. The map due to the sub peak of Li-K on the left hand side showed an increase in relative intensity with increasing charge in the anode material. The middle map in figure 11 indicates that the metallic lithium formed locally and distributed heterogeneously under the fully charged condition. The right hand side map due to C-K of the 3rd order in figure 11 indicates the intensity distribution due to graphite; the other important constituent of the anode. Under the fully discharged condition, the intensity was strongest. The intensity reduced substantially when the amount of charging increased by 30 %. However it stayed at this level, when the amount of charging increased to 100 %.

Figure 10. Two important steps are illustrated in a procedure for transferring the samples of a lithium-ion battery anode and mounting them on a sample holder of the EPMA. a) Both the sample holder and the insertion chamber were covered with a wrapper to avoid the direct contact of the sample surface to atmospheric air. b) The three samples with different amounts of charging were mounted on the sample holder side by side.

Figure 11. Three maps constructed by using the X-rays in the three energy ranges corresponding to sub peak of Li-K (left), Li-K (middle) and C-K of 3rd order (right). Each map covered an area as large as 30 x 80 mm² consisted of three samples with different amount of charging: 0 % (A), 30 % (B), and 100 % (C).

Three typical spectra corresponding to the three different conditions are shown in figure 12. Figures 12a and 12b show the spectra in the energy range between 48.5 and 59.5 eV and between 92 and 97 eV, respectively. The former energy range covers the sub peak Li-K (50 eV) and Li-K emission (54 eV) with the partially overlapped C-K of the 5th order (56 eV), whereas the latter covers...
C-K of the 3rd order. In spite of the close energy between the Li-K emission and C-K of the 5th order, these are distinguished by high energy resolution of this spectrometer. The spectra were extracted from the typical pixels observed in the three maps shown in figure 10. As shown in figure 12a, the sub-peak of Li-K and the Li-K were not observed in the fully discharged anode, whereas the sub-peak of Li-K was observed in the charged anodes at around 50 eV and the Li-K was clearly observed in the fully charged anode. The change in the intensity of the C-K the 3rd order shown in figure 12b. Additional bonding information can be observed in the shoulder around 96 eV due to the π bond in the profile of the fully charged anode. The sub-peak intensity corresponds to the charging state of the battery. It is estimated that the intercalation phenomena of Li-ion to the anode graphite layers is the meaning of Li-ion and graphite layers are interaction and bonding with ionic combination. So this distribution corresponds to the electron charging. On the other hand, metallic Li exists in the fully charged area and has a dendrite structure. C-K is decreased as the graphite layers distance is gradually expanded by the intercalation with Li-ions. Compared with TEM-SXES, this large area distribution of chemical state spectral map can be provided by EPMA/SEM-SXES.

Figure 12. Three typical spectra of a lithium ion battery anode corresponding to the three different conditions: 0 % (A), 30 % (B), and 100 % (C). a) The energy range between 48.5 and 59.5 eV covered the emission peaks of the sub-peak of Li-K, Li-K and C-K of the 5th order; and b) between 84 and 104 eV covered the one of the C-K of the 3rd order.

4.2. Trace element analysis

The WD-SXES has a very high potential for analysing trace elements in steel. With precise calibration, it is possible to extend the range of trace element analysis to very low concentrations. In the ordinary EPMA, the calibration method is usually used in the lower concentration ranges and requires a series of reliable standard specimens. The standard deviations of calibration curves determine the concentration limit as well as the accuracy of measured concentrations. With the WD-SXES, a better peak to background ratio can be obtained. Furthermore, the better energy resolution of the WD-SXES produces a more genuine target spectrum, which is well separated from overlapped spectra that often occur, and well defined background intensities resulting in the target spectra of the element of interest for the standards being very similar to that taken from the sample.

With preliminary experiments, calibration curves of boron, carbon and nitrogen in steels were obtained within the concentration range between 10 and 100 ppm by mass. The signal of each of the characteristic X-rays from the trace elements; B-K, C-K of the 2nd order and N-K of the 2nd order, could be unambiguously observed. The calibration curves for the three trace elements were linear. These straight lines indicated that the concentration range of 10 ppm by mass could be detected using this method. The results of the present experiments strongly suggest that a similar method can also be used for the analysis of trace elements in semiconductors. As shown in figure 13, the detection limit of lithium was estimated in a 5 mass% Li-Al alloy to be 80 ppm by mass using Eq. (2):
\[ D.L. = \frac{2\sqrt{2}}{\sqrt{P \times P / B \cdot t}} \cdot C\% \]  

(2)

Compared with TEM-SXES this SXES-EPMA/SEM is possible to quantify these kinds of trace elements for metals.

4.3. Ti-N overlapping

Using EDS and conventional WDS, N-K and Ti-L overlapping spectra are difficult to separate. To overcome this problem, deconvolution of the spectra is often applied. For WD-SXES, with its higher energy resolution, there is no requirement for deconvolution. For example, figure 14 shows a small TiCN grain in steel that was analysed using WD-SXES. For quantitative analysis, deconvolution is better to get more correct results. But as a primary result without deconvolution, we can distinguish the N-K peak. It is important to observe with native information, because sometimes, deconvolution include the artefact by calculation. The N-K and Ti-L peaks can be seen as clearly separated. Line step analysis was carried out with a step size of 100 nm. The N-K can be seen to be stronger on the outside edge (blue) than that of the inside (red) of the TiCN grain. The C-K intensity is the inverse than that of nitrogen.

Figure 13. Li-K and Al-L emission of 5 % Li-Al.

Figure 14. Backscattered electron image of TiCN, N-Kα, Ti-Lℓ and C-Kα spectra at the rim and core of grain. Three line analysis of N-K, Ti-Lℓ and C-K onto TiCN grain in steel.
5. Conclusion
A newly developed wavelength dispersive soft X-ray emission spectrometer (WD-SXES) with two kinds of gratings; JS50XL and JS200N have been installed on both EPMA and SEM. The spectrometer covers the energy range between 50 and 210 eV. X-rays of up to 700 eV can be detected by using higher order reflections. Experimentally the lower end of the energy range could be extended down to 46 eV. The energy resolution of this SXES was 0.2 eV which was evaluated from the Fermi-edge of the Al-L spectrum.

The valence band Li-K and ground state Li-K emission spectra due to lithium metal and lithium fluoride were observed for the first time in EPMA. The sub-peak of Li-K and Li-K emission spectra from samples of a lithium ion battery anode under different charge states were measured and mapped in an area as large as 30 x 80 mm². A clear distinction in spectra due to chemical states of lithium shows a high potential for the characterisation of lithium ion battery anodes.

For the trace element analyses of boron and nitrogen in steel, their calibration curves could successfully be obtained in the composition range between 10 and 100 ppm by mass. This method could detect their concentrations as small as 10 ppm by mass. The trace element analysis of light elements in materials other than boron and nitrogen in steel could possibly be performed at these levels of concentrations.

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