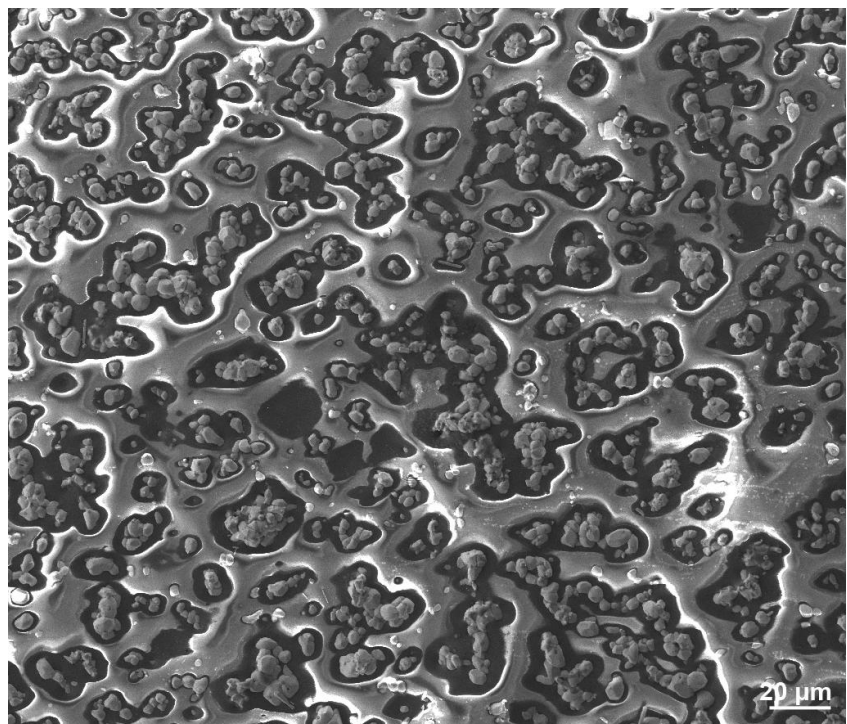


SEM/EDX ANALYSIS OF BORON



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A case study

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Introduction

In this project a qualitative analysis of boron was made using energy dispersive X-ray spectroscopy (EDX) in the scanning electron microscope (SEM). The background to this topic is that both the qualitative and quantitative analysis of light elements are not straightforward and some problems may arise, which will be discussed in this report. Also, a technique is presented which permits the detection of boron when charging effects are present.

The first stage in the analysis of an unknown is the identification of the elements present, i.e. the qualitative analysis. To make an accurate quantitative analysis it is of great importance that the elemental present in a sample have not been misidentified. Almost all commercial X-ray microanalysis software systems on the market today include an automatic qualitative analysis function. However, it is important for the operator to always confirm the identifications suggested, especially for low energy peaks.

First, the material investigated is described. Then, a brief background of the techniques used in this work; electron microscopy, energy dispersive X-ray spectroscopy and focused ion beam to make cross-sections.

Material investigated

The material investigated in this project was a (Mo,W)Si₂ based composite with boride addition. The material is in the form of rods with a diameter of 3 mm. It was of interest to study the oxidation behaviour of the material and it was therefore exposed isothermally in a furnace for 24 h in the temperature range 300 - 1000°C. The atmosphere was dry oxygen with a flow rate of 0.8 cm/s. When exposed to this environment the material forms a silica scale. In order to understand the oxidation mechanisms this oxide scale and the adjacent bulk is investigated by different techniques. The focus in this work is on the use of scanning electron microscopy with energy dispersive X-ray spectroscopy for imaging and chemical analysis of the microstructure of the bulk material and the oxidation products.

Scanning electron microscopy

The scanning electron microscope (SEM) has been a tool for imaging and chemical analysis in oxidation and corrosion research for several decades. The combination of a resolution down to around 1 nm and a large depth of focus enables a detailed study of the typically rough surfaces of oxidized samples that may be difficult to study in the optical microscope. In addition, if an energy dispersive X-ray (EDX) spectroscopy analysis system is attached to the scanning electron microscope, both qualitative and quantitative chemical analysis can be carried out. In oxidation research the SEM is commonly used for imaging and chemical analysis of the microstructure of the bulk material and the oxidation products, i.e. grain sizes, distribution of phases, surface topography, specific oxide features and cracks or pores in the oxide scale. It is possible to interpret the oxidation growth mechanisms by a detailed morphological examination combined with an investigation of the oxidation kinetics. Site specific chemical composition of the oxidation products, both crystalline and amorphous, can then be obtained with EDX. This is in contrast to XRD, which gives only crystal structure.

The principle of the SEM is as follows: an electron beam produced in the electron gun is passed through a series of magnetic lenses and apertures, which provides a focused electron beam. As the beam strikes the sample, the beam electrons interact with the atoms in the sample and a variety of signals is generated (see Figure 1). The signal of interest in this work are the X-rays for chemical analysis.

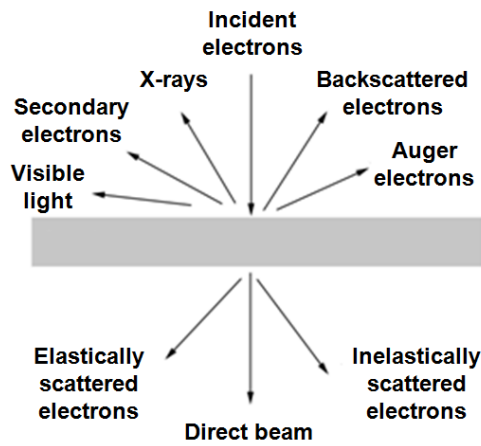


Figure 1: High energy electrons that strike a material will generate different types of signals. These signals can be used for imaging and chemical analysis.

The signals originate from different depths and volumes in the sample (see Figure 2) where the interaction volume in the sample is schematically shown. The X-rays escape from a greater depth than both secondary electrons and backscattered electrons and have the lowest resolution of the signals generated in the SEM, typically around $1\mu\text{m}$ at an accelerating voltage of 20 kV.

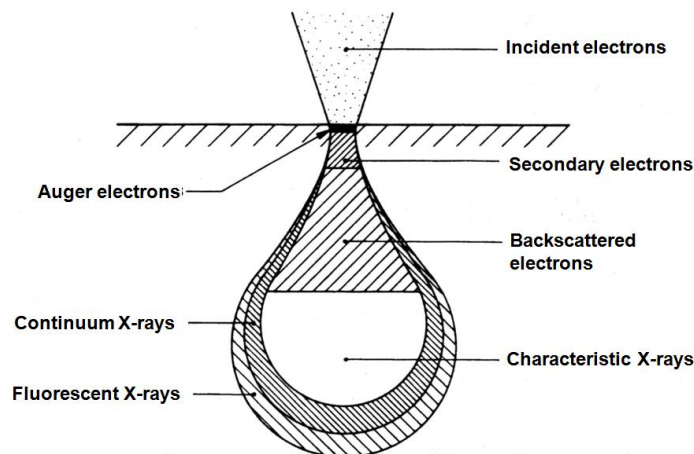


Figure 2: The interaction volume in a SEM sample showing the depth from which the different signals are generated. The interaction volume is approximately $1\mu\text{m}$ at 20 kV.

Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDX) provides chemical information about a material. When an incident beam electron strikes an atom, it may knock out an inner shell electron if the beam electron has sufficient energy. As the excited atom returns to its stable state, the excess energy is released as an X-ray photon or Auger electron. The X-rays emitted have energies characteristic for each specific atom, thus they provide chemical information about the sample.

In this work, the chemical analysis were done using an FEI Quanta 200 environmental scanning electron microscope (ESEM), equipped with a field emission gun (FEG). Because MoSi₂ based composites are multiphase materials, an accelerating voltage of 8 – 10 kV was used to decrease the interaction volume, thereby improving spatial resolution. The lower accelerating voltage also minimizes charging effects, which was beneficial since the oxide scale consists of nonconductive silica.

The EDX was used here to identify different phases present in the oxide scales. The instrument was an Oxford Inca EDX system installed on the FEI Quanta 200 environmental scanning electron microscope (ESEM). For most of the EDX analysis, an accelerating voltage of 10 kV was used in order to improve spatial resolution. This accelerating voltage was sufficient to generate elemental peaks from all of the elements in the sample. The quantification of boron in the (Mo,W)Si₂ material posed a problem because of the overlap between peaks of boron and molybdenum in the EDX spectrum. Consequently it was possible to analyze boron only in samples exposed to temperatures at which molybdenum, as a result of evaporation, is not present in the oxide scale. The low energy boron peak is also difficult to quantify, together with other light elements. For details, see next section.

Specimen preparation - focused ion beam (FIB)

To investigate both the oxide scale and the subjacent bulk material, cross-sections of the oxidized MoSi₂ samples were made. Due to the bad adhesion of the oxide scale, focused ion beam milling (FIB) was used. The oxide scales on the sample surface exhibited features with different morphology and composition. The traditional methods, such as cutting and grinding, can cause damage to the often fragile oxide scales. This is not the case with FIB milling. Also, the

technique provides cross-sections of the sample from a well defined area with interesting features. The FIB system used in this work was an FEI DualBeam Strata 235 workstation, with a liquid gallium ion source and a maximum accelerating voltage of 30 kV. The DualBeam combines the SEM and FIB, with the ion column tilted 52° from the electron column, see Figure 3. It is thus possible to use the SEM mode for imaging during the milling process. This is not as destructive to the sample surface as ion imaging would be. It may be noted that the illustration shows the stage and not the sample. In this work the cross-section was made at the end of an oxidized rod and the generated backscattered electrons thus had a free path with no edges blocking the way.

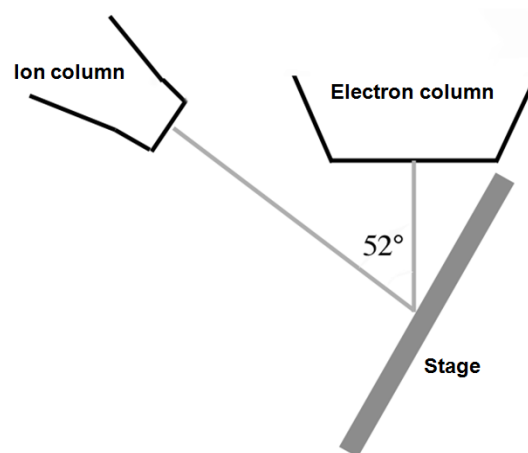


Figure 3: A schematic image of the FIB-SEM showing the electron and ion columns. The ion column is tilted 52° from the electron column.

The principle of the FIB is that ions are emitted from a liquid gallium ion source. The beam passes through a series of electrostatic lenses and apertures that focus the ion beam. Material is sputtered away when the ions hit the sample surface. The amount of material that is sputtered increases with beam current; it is possible to mill the material with varying precision by changing the ion beam current, i.e. fine milling to get a smooth surface without any re-deposition or coarse milling for fast sputtering of material.

Why is light element difficult to analyze?

Analysis of the light elements, i.e. Be, B, C, N, O and F, is difficult because of their low photon energies. Low photon energy leads to many complications such as:

- a high absorption in the specimen and in the detector
- the low energy peaks is positioned close to the electronic noise of the detection system (which can be seen at about 0 keV)
- with light element this gives a low yield of X-rays

When having a higher atomic number element this gives a spectra with more peaks and permits the use of an alternate peak if overlap in spectrum occurs in the specimen.

The high absorption in the detector results in a incorrectly measurement of photons and consequently a shift in the peak position.

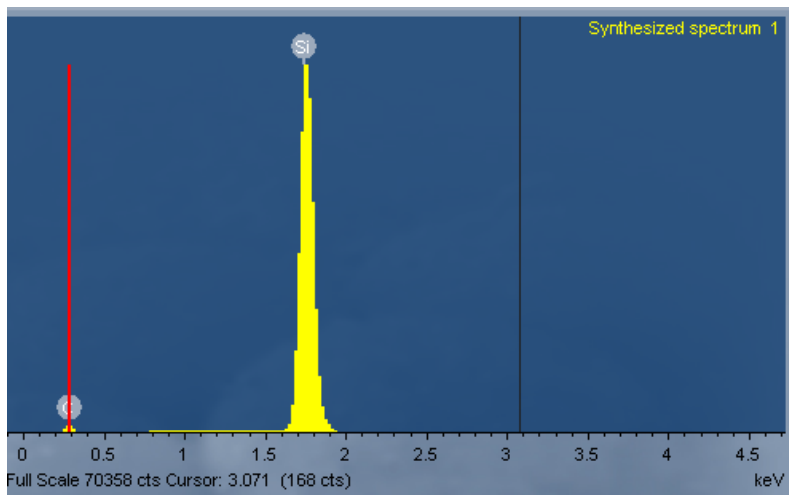
How does different accelerating voltage influence?

Analysis of the light elements is more difficult due to the strong self-absorption these low energy X-rays undergo in the specimen. As the beam energy is increased, the X-ray range increases. Although more light element X-ray intensity is generated within the specimen due to higher overvoltage, X-ray absorption increases more rapidly due to the greater depth over which these additional X-rays are produced. Thus, if we measure the X-ray intensity for oxygen in various matrices, starting at low beam energy (2keV) and increasing in steps to 30keV, the oxygen K intensity is seen to initially rise, reach a peak and then decrease with further beam energy increases. Due to absorption effect on light element X-rays the analysis is not optimized for low energies.

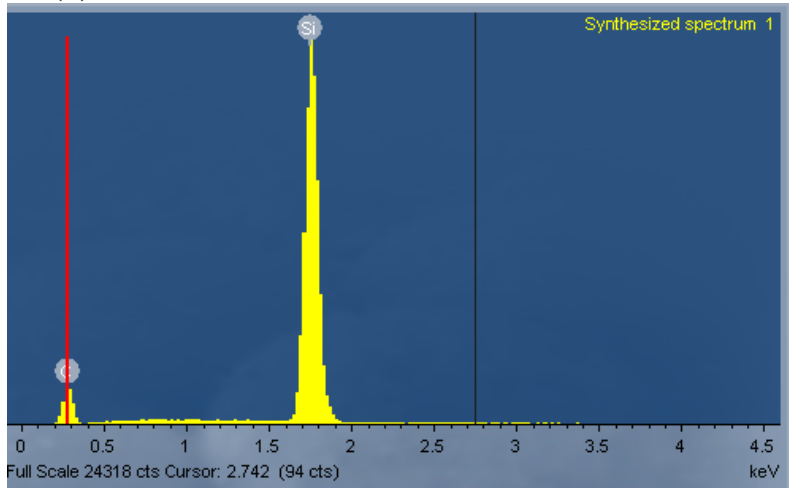
The influence of absorption is illustrated in Figure 4, which shows an EDX spectrum of SiC. It may be noted that in an EDX spectrum the X-ray intensities can be seen on the vertical axis and the X-ray energies on the horizontal axis. At the high beam energy of 20keV, see Figure 4 (a), the C peak intensity is greatly reduced by absorption relative to the Si K peak. The C peak could easily be missed, although it represents 30 wt.% of the specimen. At 10 keV the peak is more visible, see Figure 4 (b) and at 5keV the C peak is easily detectable, see Figure 4 (c). If a beam energy of

10keV and higher is used in order to detect heavier elements, one must therefore be particularly careful to evaluate the possible contribution of the light elements to the spectrum and it might be useful to lower the beam energy to fully confirm their presence or absence. The relative intensities may also depend on the over voltage for the two peaks, i.e. $E(\text{acc}) / E(\text{peak})$. This will affect the X-ray yield and give more Si-signal than C-signal for 20keV.

(a) 20keV:



(b) 10 keV:



(c) 5 keV:

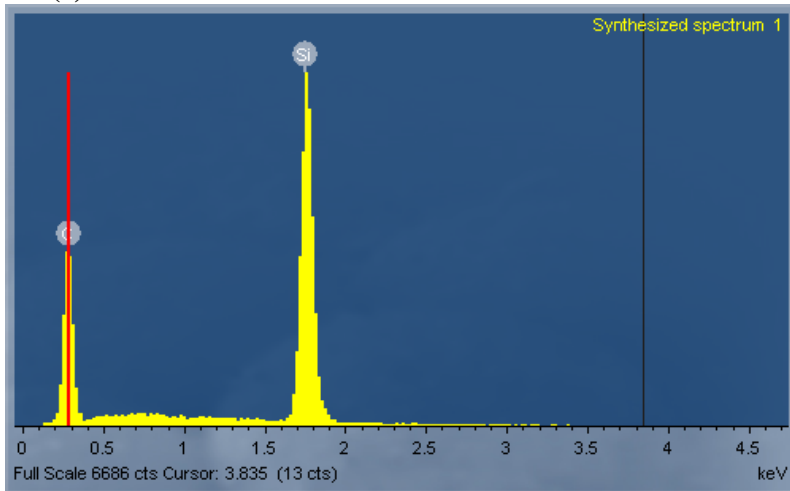


Figure 4: EDX spectra of SiC for different accelerating voltages. The carbon peak is easily detectable at lower accelerating voltages.

Family of X-ray peaks

An important concept is that of the family of X-ray peaks. When the beam energy exceeds the critical energy needed for ionization of a particular shell or subshell, this will produce a family of peaks. The exception is of the atoms where $Z \leq 9$ where only the K peak is present. With a beam energy of 20 keV all possible peaks of an element in the range 0.1 to approximately 15 keV will be excited with increasing efficiency as the photon energy decreases. When one detects all possible members of a family of peaks in the spectrum, this supports the identification of that element. Because the family members must all exist, the absence of a particular peak should raise suspicion that the element is not identified correctly.

As EDX has a relatively poor energy resolution this leads to frequent peak overlaps as well as the inability to separate the members of the X-ray families that occur at low energy (< 3keV). The K peaks of the light elements (beryllium, boron, carbon, nitrogen, oxygen) occur in the X-ray energy range below 1keV. A major consideration in EDX below 1keV is the problem of interferences between K peaks for light element and L- and M-family peaks of heavier elements. This is the case with the analysis of the oxidized MoSi₂ material. Since the K peak for boron overlaps with the M peak of molybdenum, it is impossible to qualitatively identify B on samples

where Mo is present. In this work boron could be detected on the samples oxidized at 1000°C since Mo is not present there due to evaporation.

The qualitative EDX analysis performed in this work

For EDX quantification of these features an accelerating voltage of 10 kV was used since this was sufficient to generate all elemental peaks of interest. In order to optimize the chemical analysis of boron in silica present in the samples, the analyzer mode in the INCA software was used to find the optimal choice of accelerating voltage. In Figure 5 the different steps in this optimization process is shown. First, the analyzer mode was chosen and the button “spectrum synthesize”, see Figure 5 (a). An accelerating voltage of 20 kV was chosen and the formula in atomic %. The spectrum shown in the image is the synthesized spectrum for these options.

In Figure 5 (b) the synthesized spectrum for an accelerating voltage of 4 kV is seen. It is clear that with a lower accelerating voltage, the boron peak is much stronger compared to the other peaks. A lower accelerating voltage is clearly preferred. It is possible to go even lower in accelerating voltage. However, as the beam current also diminish, it was found that 4 kV was the optimum choice for this analysis. The spatial resolution is also better at lower accelerating voltages.

(a)

The screenshot displays the INCA - Analyzer software interface. The main window is divided into several sections:

- Navigator:** A vertical flowchart on the left side showing the workflow steps: Project, Sample, Microscope Setup, Acquire Spectra, Confirm Elements, Quant, and Report. The 'Spectrum Synthesis' step is highlighted with a red circle. A red arrow points to the 'Analyzer' icon at the bottom of the Navigator.
- Data:** A section on the right side of the Navigator, currently empty.
- Spectrum Synthesis:** The main workspace on the right, containing:
 - Acquisition/Geometry:** Parameters for data collection, including Process time (5), Livetime (100.00), Number of channels (1k), Spectrum range (0 - 20 keV), Probe current (0.100 nA), and Accelerating voltage (20.00 kV).
 - Spectrum Plot:** A graph showing a synthesized spectrum with two prominent peaks. The x-axis is labeled 'keV' and ranges from 0 to 3. The y-axis is labeled 'Full Scale 21485 cts'. A cursor is positioned at 2.011 (173 cts).
 - Element Selection:** A periodic table of elements with checkboxes for selection. The formula B2SiO5 is entered in the 'Formula' field.
 - Concentration (%):** A table showing the calculated concentrations for the selected elements:

| Element | Concentration (%) |
|---------|-------------------|
| B | 25.0 |
| Si | 12.5 |
| O | 62.5 |

(b)

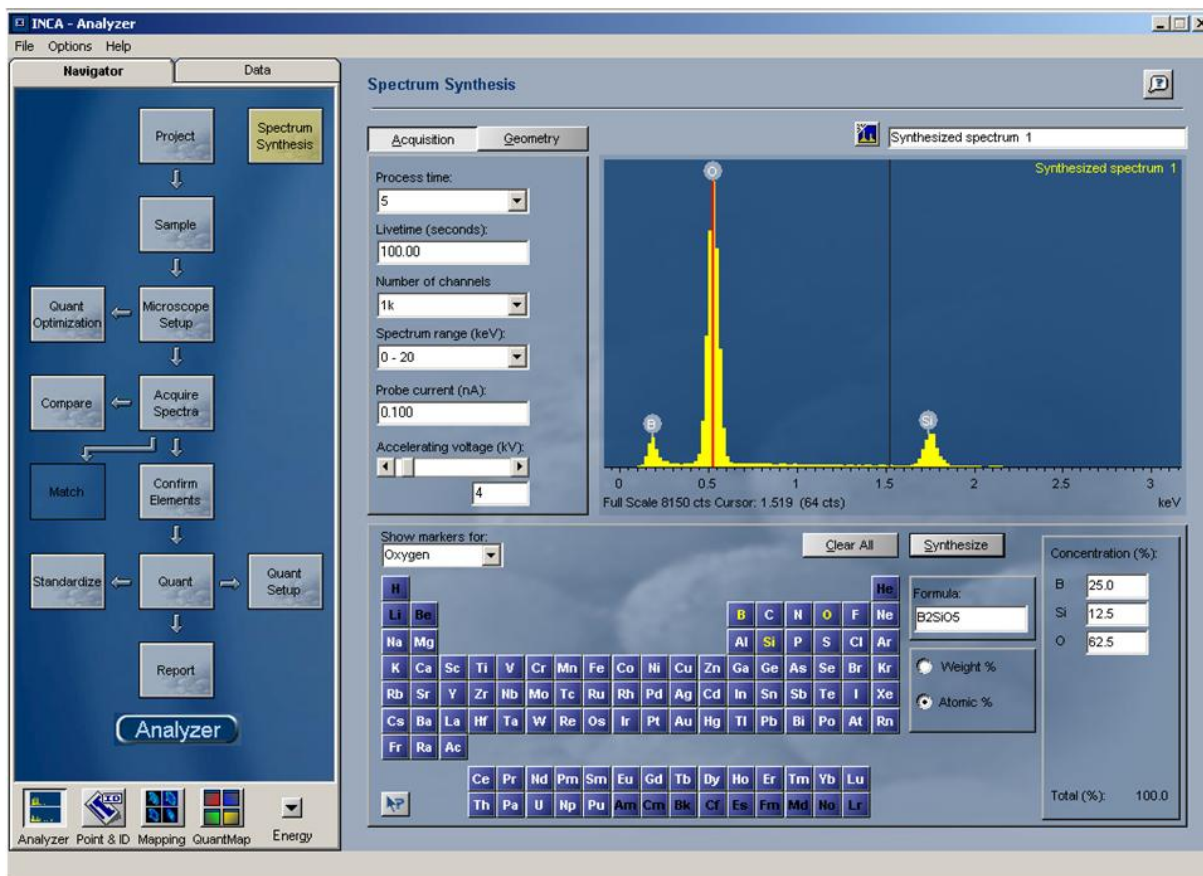


Figure 5: Using Spectrum Synthesize in the INCA software to find the optimum accelerating voltage to detect boron.

In this work the oxide scale formed on the exposed MoSi_2 material was of interest. The oxide scale consisted of nonconductive silica. In order to analyze it, together with the adjacent bulk, one sided cross-sections were made (see the FIB section). As previously mentioned, there are overlap between the boron and molybdenum peaks. Therefore, the boron cannot be identified when molybdenum is present in the oxide scale. In this work boron could only be detected on the samples oxidized at 1000°C , since Mo is not present at that temperatures due to evaporation. Figure 6 shows a SEM cross-section image of a sample exposed at 1000°C . The oxide scale consists of SiO_2 with some B_2O_3 . When imaging the oxide scale in Figure 6 using secondary electrons, the presence of a duplex scale is visible, see Figure 7.

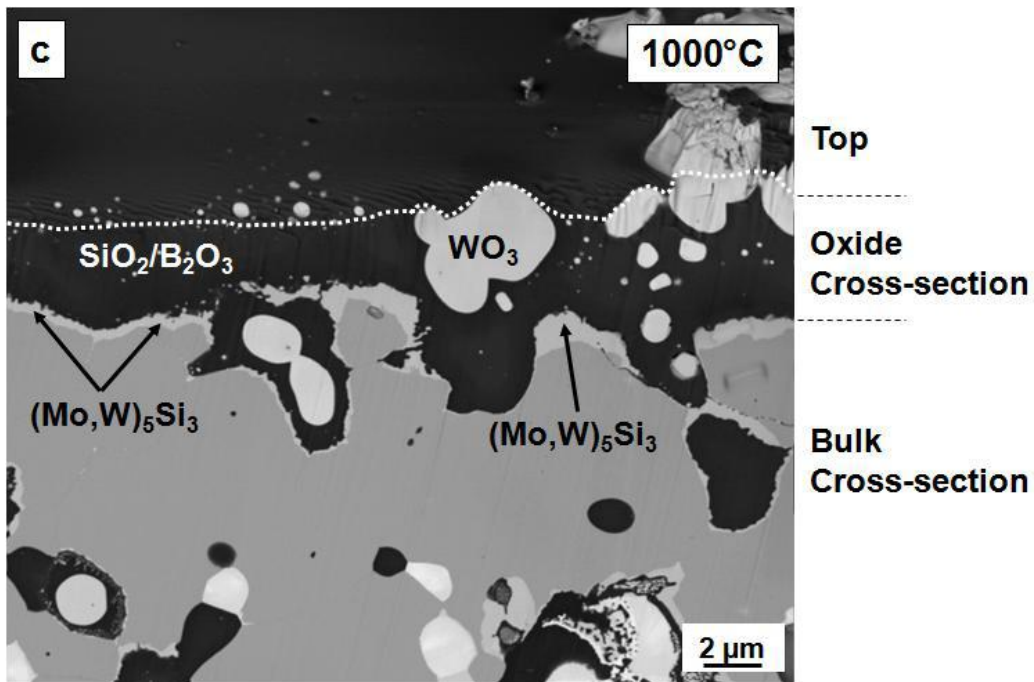


Figure 6: A SEM cross-section image showing the microstructure of the oxide scale formed on the (Mo,W)Si₂ based composite with the addition of boride. The sample is exposed at 1000°C.

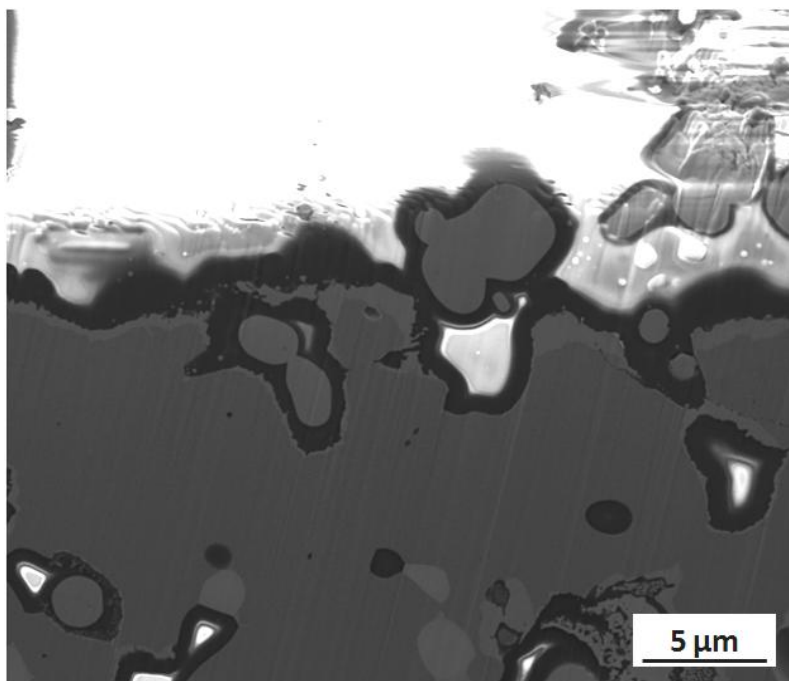


Figure 7: A SE image showing the cross-section of the sample exposed at 1000°C. The oxide scale is observed to be duplex with a brighter top layer and a darker bottom layer.

The task in this work was to make a qualitative analysis of this oxide scale. Due to the charging effects, it was not possible to use “point and id” in the INCA software. The sample drift made the electron beam change position and the results of the analysis showed misleading composition of the oxide scale. There were signals from adjacent regions which made a correct analysis impossible.

In order to overcome this problem, a different approach was used. First, the analyzer mode in the INCA software was used. Choosing the “Acquire spectrum” box makes it possible to acquire a spectrum. When using this selection the program will acquire a spectrum of the whole frame. Since it is of interest to investigate the different parts of the duplex scale in Figure 7, a smaller window was selected. This is illustrated in Figure 8 with the red and blue boxes. The INCA program will acquire a spectrum from the whole region within the frame and analyze this region.

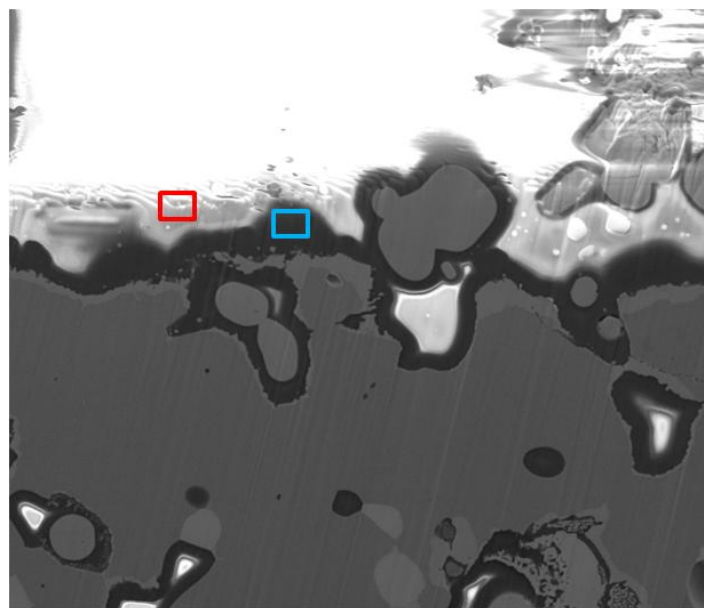


Figure 8: A smaller frame was chosen in the INCA program in order to acquire a spectrum from a smaller area.

Due to charging effects the sample drifts and this motivated the second step in the analysis that was made. If nothing was done the drift would move the electron beam into another region and the analysis would be incorrect. Therefore, the shift X and shift Y knobs were used in order to

move the electron beam simultaneously as the sample drifted. By moving the electron beam, it remained in the upper part of the oxide scale and the spectrum could be acquired. Then the same could be done for the lower part of the oxide scale. The upper part showed a boron content of about 15 at.% while the lower parts consisted of 5 at.%.

In this work a qualitative study of the oxide scale showed a silica scale with boron. It was no doubt that it consisted of boron with a high boron content in the upper part of the oxide scale and a lower boron content in the lower part. However, in order to get the exact composition of the oxide scale, a reference material with a known boron content is needed for calibration.

Conclusions

This study has shown that it is possible to analyze boron by the use of SEM/EDX. The EDX quantification was based on the following principles:

- optimizing the accelerating voltage so that a strong boron peak, and a high spatial resolution, is achieved
- check that there is no overlap between peaks of boron and other elements in the EDX spectrum
- performing the drift control manually since the sample exhibited charging

The EDX quantification provided a rough estimate of the composition of the boron containing silica and for this study that was an acceptable result. For a more precise value of the composition, a reference material would be required.