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APPLICATION NOTE

Characterization of complex refractories for steel production using the Axia ChemiSEM

Introduction

Refractories are composite materials employed in the manufacturing industry in many fields due to their high temperature and corrosion resistance. One of their main applications is in steel production as protection in heating furnaces, refining vessels, and to contain the flow of molten metal.

Refractory oxides experience extreme working conditions, including corrosive environments and high temperatures (liquid metal temperatures exceed 1,650°C). Corrosion and erosion processes occur by contact with molten metal, liquid oxide slag, and abrasive surfaces, having a notable impact on the stability of the refractories during their service and, possibly, leading to a reduced service life.

For this reason, the physical and chemical properties of the materials employed are very important for the stability and wear resistance of the refractory product during use, hence making proper material selection crucial. Most of the refractories are fabricated by combining many different material types, such as ceramic (oxide) powders, reactive metals, or carbides, and sometimes carbon/graphite flakes to form the final product.

Figure 1. Refractories are used to contain the molten steel.

Large-scale overview of complex refractories

The materials characterized in this application note may be employed in pressed bricks, monolithic linings, or carbon-bonded products such as the stopper rod and submerged entry nozzle for continuous casting of steel.

The refractory mixture contains zirconia mullite (ZM), brown fused alumina (BFA), and fine-grained fused silica. For the purpose of this study, the different grains have been mounted in epoxy and polished.

A large area of the polished section has been characterized to provide an overview of the distribution of the different materials. A conventional approach would provide either a backscattered electron (BSE) image or a secondary electron (SE) image, but these would not disclose the composition of the grains. In fact, the information provided by the BSE contrast, where the grayscale levels change according to the average atomic number of the material, is not enough to distinguish the different phases and possible contaminations within this mixture of complex refractories.

In this application note, we present a new approach to elemental analysis, which, in a scanning electron microscope (SEM), is commonly provided using energy dispersive X-ray spectroscopy (EDS). The new approach using the Thermo Scientific™ Axia™ ChemiSEM is no longer guided by the information retrieved from the SEM image. Instead it is based on the elemental information that, with the new ChemiSEM workflow, comes in combination with the SEM image (either BSE or SE image) and is displayed instantaneously.

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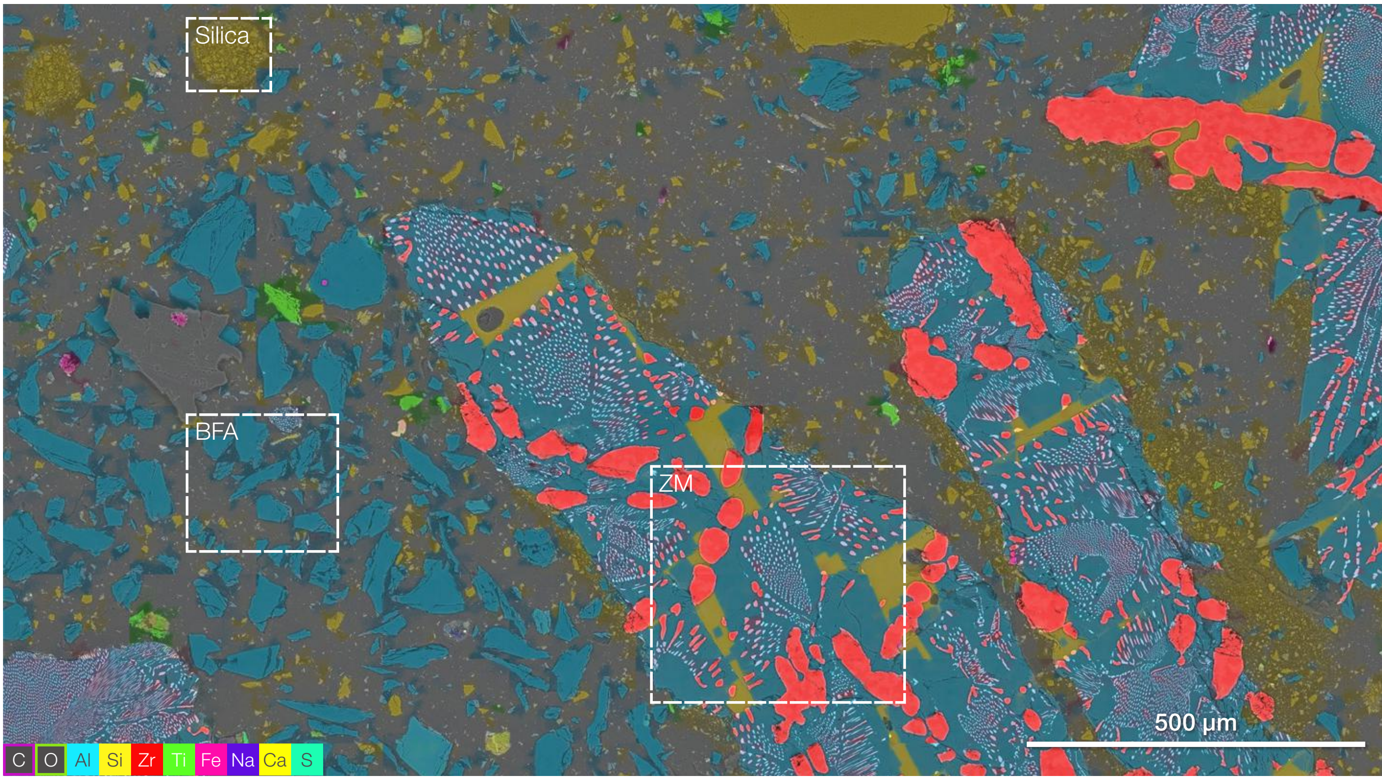

Figure 2. A modern refractory system often contains a range of different grain materials to achieve the desired properties. Being able to easily unravel the different materials distribution is important. The three boxes highlight the ZM, BFA, and fine-grained silica grains (acc voltage 15 keV, beam current 0.85 nA).

Figure 2 shows a ChemiSEM large-area overview with a field of view of more than 2 mm. The overview has been acquired by combining neighboring frames while collecting the EDS signal for each of the single frames, which has then been processed in order to provide quantitative information.

As a ChemiSEM map, it provides chemical information on the distribution of the different elements within the scanned area, allowing for the different refractories to be discriminated. In addition, the possibility to discover unknown elements in the analyzed area brings a fast and easy way to detect contaminants.

Notably, the total acquisition time of the large-area overview map ranges from 20 to 30 minutes (depending on the beam current applied and on the number of frames summed for each ROI in order to increase the EDS signal), allowing for relevant time saving.

The three different materials (ZM, BFA, and fused silica) are highlighted in the image.

Zirconia mullite

Zirconia mullite (ZM) compounds are commonly used as a raw material in refractory products due to their excellent properties. Zirconia has a high refractoriness (Tmelting = 2,715°C) and an exceptional corrosion resistance against slags. In addition, both zirconia and mullite ($Al_2O_3.SiO_2$) have lower thermal expansion coefficients than the more common alumina or magnesia, thus ZM is utilized in thermal shock-prone applications, such as continuous casting nozzles. It is produced by fusing zircon sand ($ZrO_2.SiO_2$) and alumina (Al_2O_3) in an electric arc. After fusion, the liquid oxide is cooled, and pure ZrO_2 partitions out of the lower melting point mullite matrix.

The large-scale overview in Figure 2 has been used as a map to guide further characterization of the different refractory materials.

Figure 3 shows the main advantage of a ChemiSEM image over a conventional BSE image: the BSE detector's compositional contrast provides only part of the information needed to disclose the different phases in the ZM. However, the contribution of the quantitative elemental information coupled to the SEM image allows us to achieve a complete characterization within one minute with a reduced number of steps required, as compared to a conventional EDS workflow.

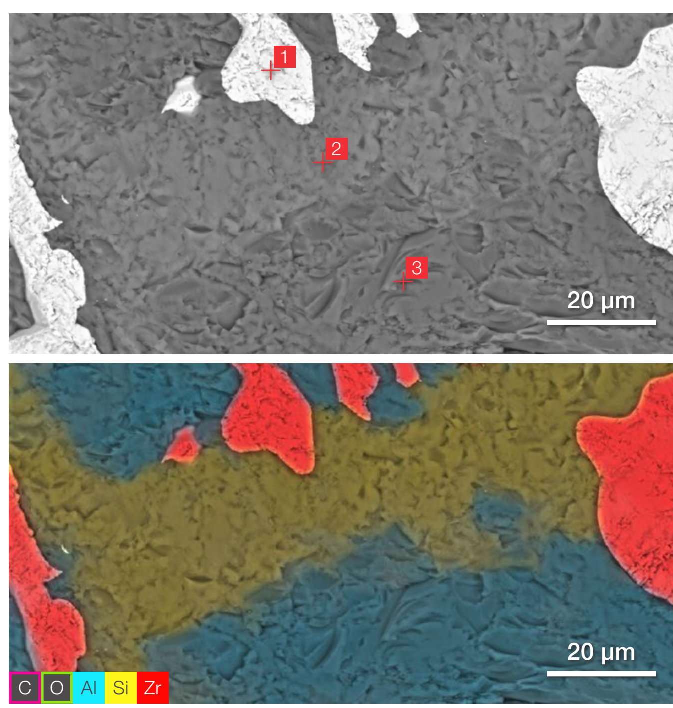

Figure 3. BSE image of ZM (top) and related ChemiSEM image (bottom) (acc voltage 15 keV, beam current 0.44 nA, acquisition time 60 s).

The distribution of the different elements can be made more evident by selectively visualizing them. The ChemiSEM images in Figure 4 that show Zr, Al, and Si distribution have been saved after the first SEM image acquisition with no need to re-acquire or further process the EDS data.

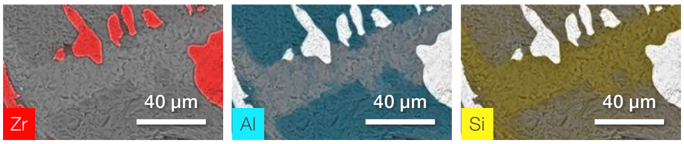

Figure 4. ChemiSEM image showing the Zr, Al, and Si distribution. The other elements have been hidden for a clearer view of the element of interest.

Point analyses and linescan confirm the presence of three phases: the zirconia, a silicate phase, and the mullite. The results of the point quantifications are presented in Table 1. 30-second point analyses have been acquired in the points marked in Figure 3 as 1, 2, and 3. The linescan in Figure 5 has been acquired on a different area.

Element	Point #1	Point #2	Point #3
O	61.2	57.3	56.1
Zr	38.8	-	-
Al	-	8.0	33.9
Si	-	32.1	10.0
Na	-	2.6	-

Table 1. Results of the point quantifications (Atomic %).

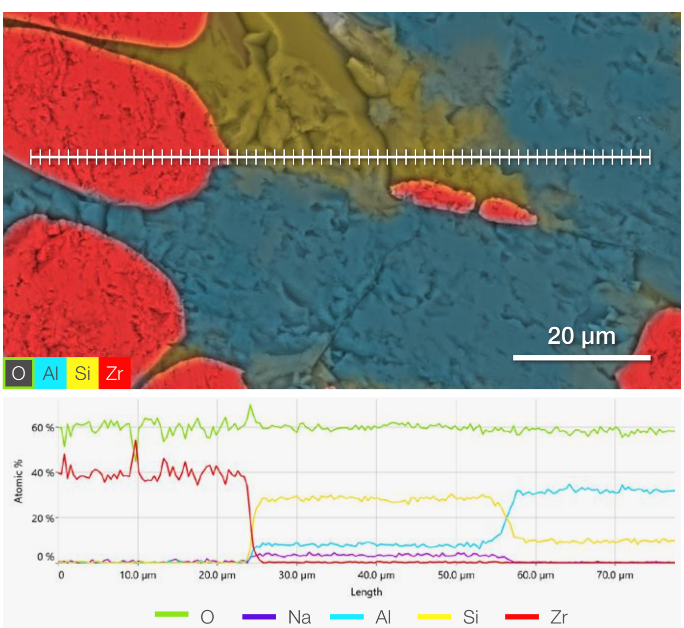

Figure 5. ChemiSEM image showing the position where the linescan has been acquired (top). A 400 s linescan acquired at 15 keV and 0.44 nA beam current (bottom).

Between the zirconia and the mullite phases, a different phase, rich in silicon (Si), is identified. This contaminant oxide phase is primarily composed of silicon (Si), along with smaller amounts of aluminum (Al) and sodium (Na). Sodium should not be present in the ZM; however, it could have been added to aid the melting. It is not meant to become part of the product, because, as happened in our case, it became incorporated into the material, generating an impurity phase.

Another possible explanation of the presence of sodium is related to the source of alumina employed during the production of the ZM. White fused alumina (WFA) is one of the possible alumina sources, and it is likely to contain a small amount of sodium, approximately 0.1%. The sodium, in fact, is employed in the Bayer process to refine the alumina from the bauxite (discussed later in this app note).

Brown fused alumina

Brown fused alumina (BFA) is used in many refractory applications, such as bricks, monolithic, and carbon-bonded nozzles for continuous casting. Bauxite is the ore used for production of alumina and aluminum, and it consists of aluminum hydroxides along with a range of impurities (Na, Ti, Fe, and Si). The reason is that bauxite ores are naturally mined with hematite (Fe_2O_3), kaolin clay, anatase (TiO_2), and ilmenite ($FeTiO_3$).

The refinement of alumina from bauxite first occurs through dry separation, then through the Bayer process. The latter consists of dissolving the ores in sodium hydroxide in order to remove the majority of the impurities. This alumina product can then be fused via electric arc furnace into BFA, or white fused alumina, which is the more refined, more expensive version of BFA.

A characterization similar to that performed on the zirconia mullite was performed on the BFA.

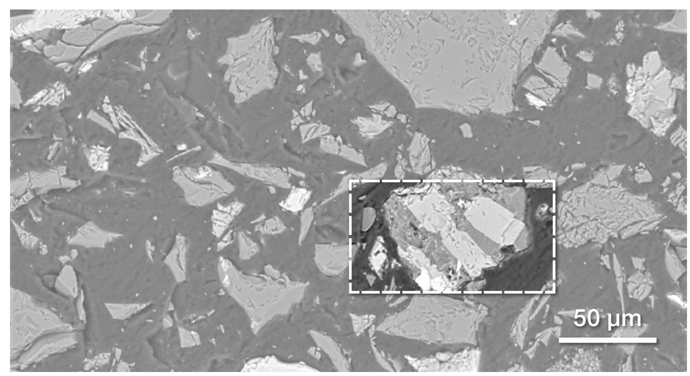

Figure 6. Low-magnification BSE image of BFA.

Figure 6 shows how the BFA typically looks when imaged in an SEM. BSE imaging has been used as the main point of this characterization to highlight any compositional differences and discover the presence of possible contaminants from the bauxite ore. The image shows the presence of different materials, given the different grayscale levels. In particular, one of the grains (marked with a white box), appears to contain different phases.

The ChemiSEM characterization presented in Figure 7 provides an intuitive distinction between the different elements, giving the opportunity to discover the presence of contaminants.

Figure 7. ChemiSEM image acquired at 15 keV (beam current 0.44 nA, acquisition time 60 s).

By selecting the elements of interest, you can immediately find the presence of at least three phases: the first phase is a Si-Al and Na-rich material (distribution shown in the first row of Figure 8), the second phase, intertwined with the first, can be identified as titanium oxide (TiO_2), while the smaller grain contains Fe and S.

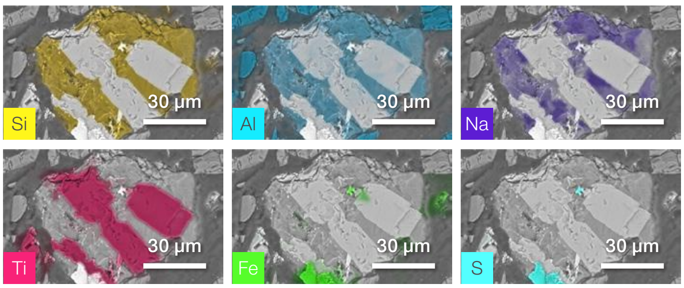

Figure 8. ChemiSEM images of the impurity shown in Figure 7.

Given the speed of the analysis, and as no post-processing is required to obtain quantitative information, another unique impurity has been imaged and characterized.

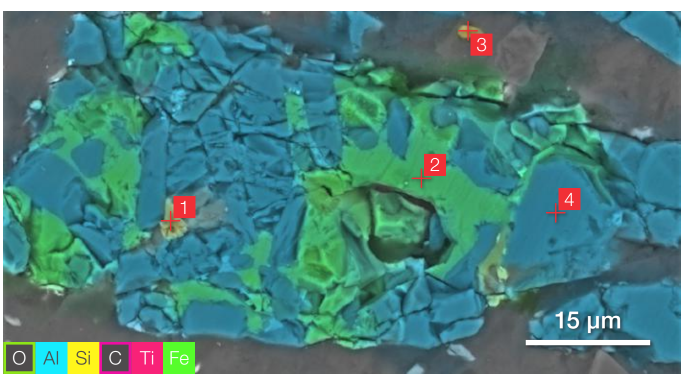

Figure 9. ChemiSEM image (acc voltage 15 keV, beam current 0.44 nA, acquisition time 60 s).

The distribution of the carbon and oxygen are hidden to avoid possible confusion with the overlay of the different colors and to give more clarity to the other elements. As for the ZM, different point analyses have been acquired in the points marked in Figure 9.

Point quantifications in Table 2 confirm the presence of contaminants within the main phase, alumina, which is identified in point 4. Silica, Al-Fe oxide, and ilmenite ($FeTiO_3$) are also found.

Figure 10. Refractory bricks line this ladle of molten steel at temperatures higher than 1,550°C while being corroded by slag.

Element	Point #1	Point #2	Point #3	Point #4
O	51.9	47.8	66.5	55.0
Al	1.1	32.5	-	45.0
Si	-	-	33.5	-
Ti	24.0	1.1	-	-
Fe	23.0	18.6	-	-

Table 2. Results of point analyses (Atomic %).

Conclusion

The steelmaking process is one of the main applications in which refractory materials are employed. It involves a range of conditions with extreme working environments, therefore requiring that the refractories maintain a high level of performance during their service lives.

Excellent resistance to corrosion and high thermal shock resistance are the main requirements for the refractory linings and shaped products. To guarantee those specifications, a variety of materials are commonly employed.

Before their use, characterization of the different materials is important to clarify the distribution of the phases within the final composite. In addition, each of the materials characterized can have different type of contaminants, dependent upon their manufacturing processes.

Using the Axia ChemiSEM's novel approach to chemical identification with its "always on" chemical analysis, discovery of unknown elements and materials makes characterization fast and easy.

Find out more at **thermofisher.com/Axia-ChemiSEM**