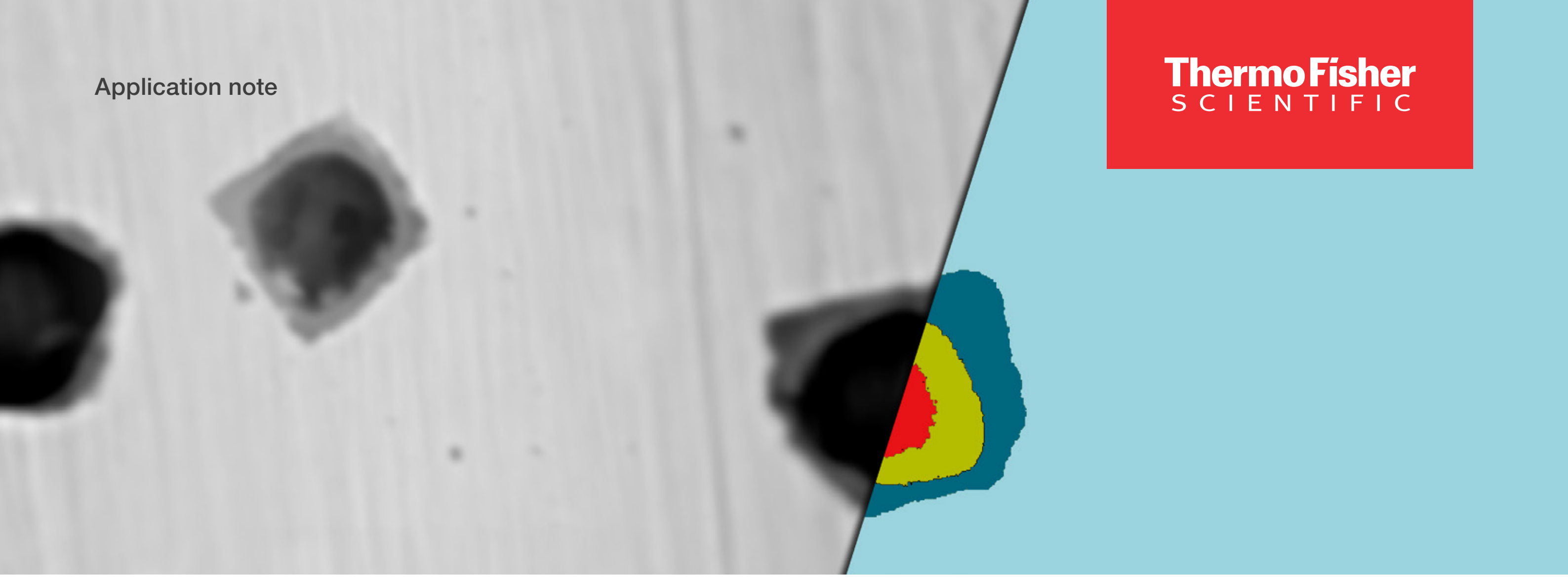
Application note



Automated SEM-EDS analysis and phase mapping of complex oxide-sulfide-nitride inclusions in steel

Introduction

Molten iron is a nearly universal solvent, and can easily dissolve metals like chromium, molybdenum, and tungsten to make a variety of valuable alloys. This behavior can, however, be a double-edged sword, as elements like oxygen, sulfur, and nitrogen must be carefully controlled when turning raw iron into steel. These light elements have low solubility in the alloyed steel, instead forming undesirable reaction products (i.e., inclusions) during refining and hot rolling. The resulting oxide, sulfide, and nitride micro-inclusions cannot be removed by simple flotation and thus become a permanent part of the final steel, affecting its mechanical properties and quality.

Production of molten steel involves very high temperatures and highly oxidizing conditions. Integrated blast-furnace/ oxygen-furnace and electric-arc-furnace scrap-melting routes both result in several hundred ppm of dissolved oxygen in the raw steel. Deoxidizers such as manganese, silicon, aluminum, titanium, and calcium may be added to reduce or control this dissolved oxygen content. The Ellingham diagram for the formation of oxides indicates which of these elements form the most stable oxides, ranked here from highest to lowest oxide stability at steelmaking temperature:
$CaO > Al_2O_3 > TiO_2 > SiO_2 > MnO$.

Control of oxygen by manganese and silicon reduces dissolved oxygen to around 50 ppm through the formation of manganese silicate inclusions. Further deoxidation by aluminum can reduce dissolved oxygen to just a few ppm, converting all oxide inclusions to micrometer-sized Al_2O_3. In some cases, it is desirable, or even necessary, to further modify the inclusion population.

Calcium additions on the order of 20 ppm can be used to lower the melting point of the inclusions (for castability), or to react with dissolved sulfur in the steel, forming a new population of calcium sulfides. Micro-inclusion populations may also contain nitrides, as titanium is often used as a getter for nitrogen, forming titanium nitride.

Overall, this can result in a highly complex mixture of inclusions; obtaining a quantitative understanding of the steel composition is vital for its controlled optimization. This application note highlights the automated analysis of complex oxide-sulfide-nitride compound inclusions in steel with scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). This approach provides a critical combination of imaging and elemental analysis, offering an accurate overview of the inclusions in steel.

Methods and results

Automated inclusion analysis was conducted on a steel sample with the Thermo Scientific™ Axia™ ChemiSEM™ Scanning Electron Microscope in order to reveal the chemical composition and size distribution of non-metallic particles found in the sample after casting and rolling. Integrated Thermo Scientific Perception Software enables rapid particle detection and classification with EDS. The aim of this analysis was to characterize inclusions >2 µm in diameter over a 60 mm^2 area of polished steel. Iron and oxygen were excluded from the analysis, for simplicity.

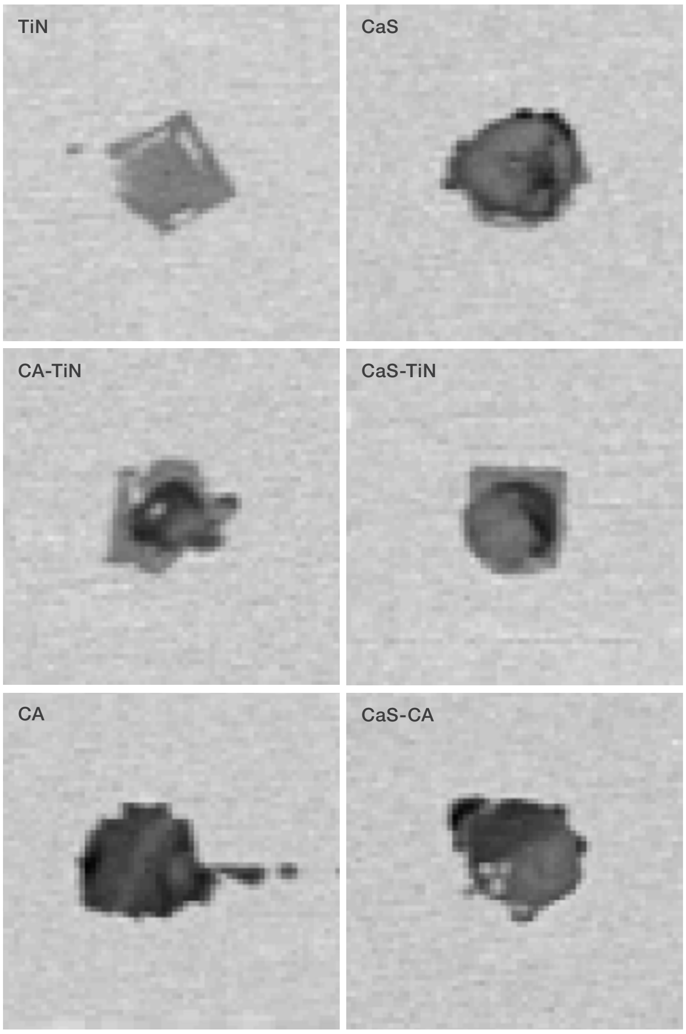


Figure 1. From Perception Software, automated BSE images of different inclusion types, with sizes ranging from 6 to 10 µm.

Aluminum deoxidation, titanium stabilization of nitrogen, and calcium treatment produced a unique distribution of compound inclusions in this steel. Figure 1 shows automatically captured backscattered electron (BSE) images of the three main inclusion types (TiN, CaS, and CA or calcium aluminate) as well as their combinations. These inclusions appear darker in the BSE images than the bulk metal

As the particles were measured, EDS data was collected for each inclusion; particles could subsequently be classified by their composition and shape.

A total of 3,888 inclusions were characterized and are shown in the ternary diagrams (Figure 2) and classification table (Figure 3).

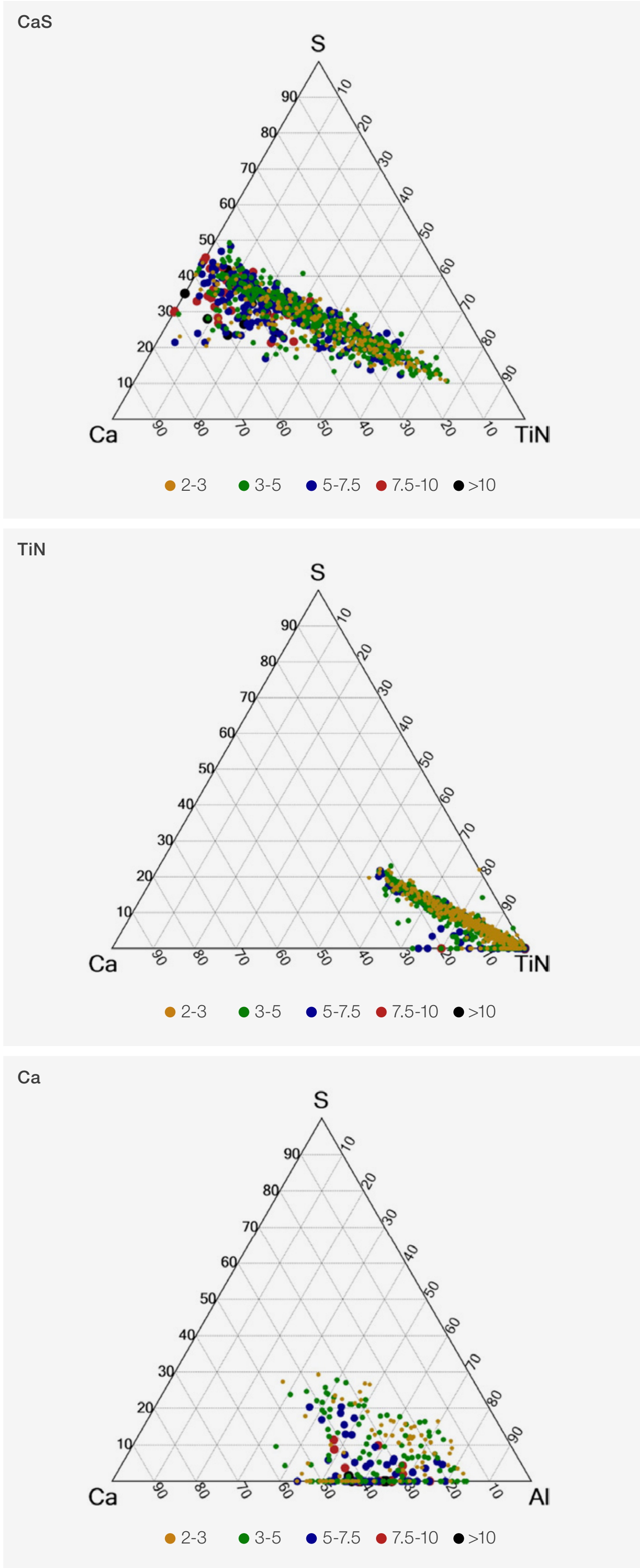
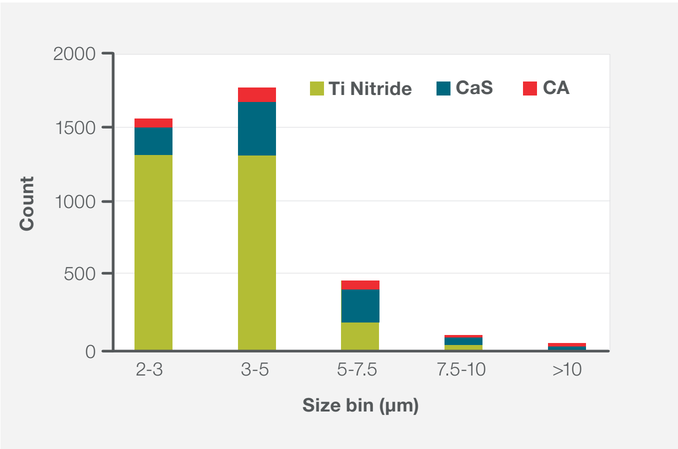


Figure 2. Ca-TiN-S and Ca-Al-S ternary diagrams reveal the composition and size distributions for the three different inclusion classes.

Rather than discreet compositional “islands,” there are instead continuous distributions between two types of inclusions on each Ca-TiN-S diagram. This indicates that the elements do not form a solid solution, but rather one compound is precipitated on top of the other. The calcium sulfide (or calcium aluminate) inclusions are formed during ladle refining, and the titanium nitride forms later by segregation during casting. The oxide and sulfide inclusions act as heterogeneous nucleation sites where the nitrides are encouraged to form at the solidification front.



	Total	2 ≤ X < 3	3 ≤ X < 5	5 ≤ X < 7.5	7.5 ≤ X < 10	X ≥ 10
Ti Nitride	2,796	1,344	1,225	194	26	7
CaS	831	180	374	221	43	13
CA	261	73	116	52	12	8

Figure 3. Particle size histogram and classification table for the three different inclusion classes.

Two inclusions were selected for further investigation. Figure 4 shows their automatically captured BSE images and EDS compositions in atomic percents. Both inclusions contain a dark core, and a lighter-colored cubic shape on the exterior, which is consistent with TiN. The main difference in composition is that the sulfur content is higher in particle B. At this point it is not clear from the images if the sulfur is associated with an oxide phase, sulfide phase, or both.

Thermo Scientific ChemiPhase Software is a novel phase identification and quantification engine for the Axia ChemiSEM System. ChemiPhase analysis provided novel insights into the steel inclusions shown in Figure 4, statistically assessing the number of phases present, their composition, and their area fractions.

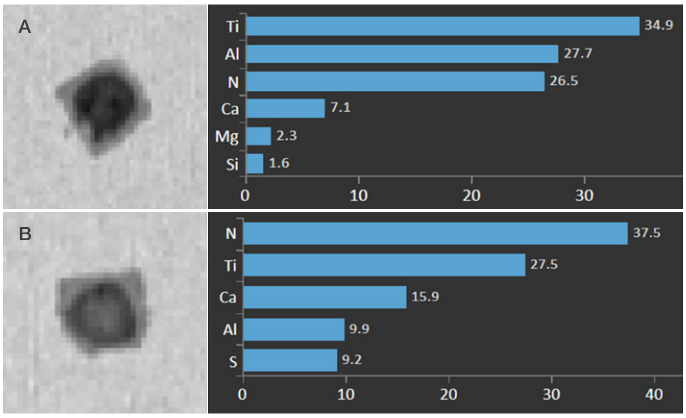
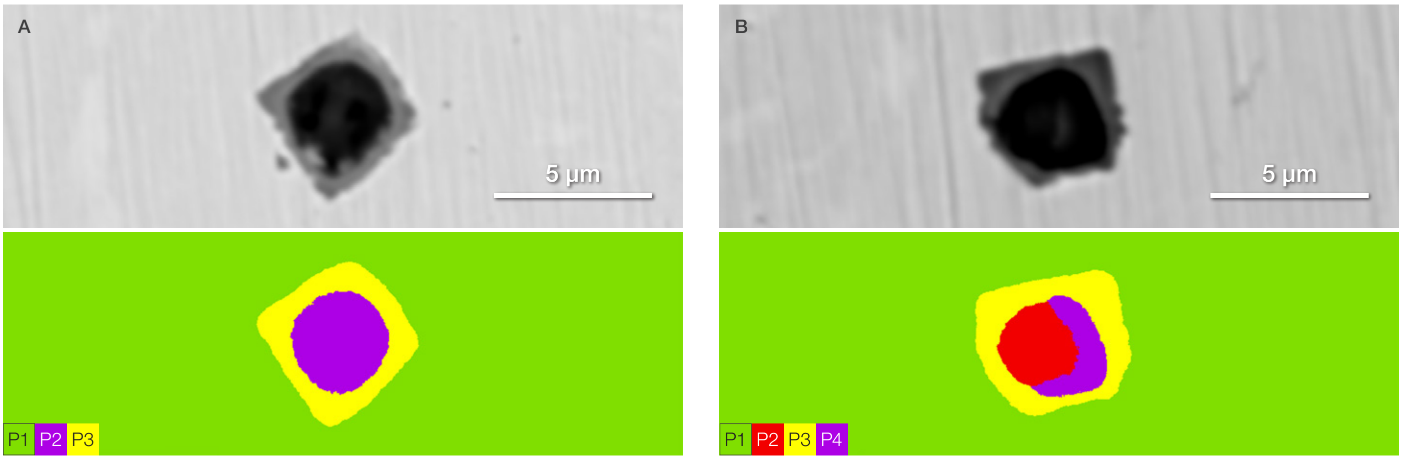


Figure 4. Perception automated BSE images and compositions are shown for two selected inclusions.

Figure 5 shows the BSE images, ChemiPhase analysis maps, and associated phase-area fractions for the evaluated regions. Results confirm that particle A has two inclusion phases present, and that particle B has three phases. The TiN area is consistent between the two inclusions, and the core inclusion (oxide and sulfide) is slightly larger in particle B (7.6 vs 7.0 µm^2). Critically, ChemiPhase analysis distinguished that the core of particle B has two parts, CaS and a Ca-Al oxide, whereas the BSE image suggested that there was only one.



Name	Area (µm^2)	Area (%)
P1- Steel	270.9	94.7
P2 - Ca-Al oxide	7.0	2.4
P3 - TiN	8.3	2.9

Name	Area (µm^2)	Area (%)
P1- Steel	269.8	94.2
P2 - CaS	4.4	1.6
P3 - TiN	8.8	3.1
P4 - Ca-Al oxide	3.2	1.1

Figure 5. Manual BSE images, ChemiPhase analysis maps, and phase-area fractions of two inclusions.

Conclusions

A large dataset containing images, spectra, as well as size and compositional information for 3,888 inclusions (>2 µm in size) was collected automatically with Perception Software on an Axia ChemiSEM System. The composition of these inclusions varies greatly and consists of calcium, aluminum, titanium, sulfur, nitrogen, and oxygen. Review of the data using custom ternary diagrams suggests that there is a continuum of particle compositions between CaS and TiN.

ChemiPhase analysis confirmed the composition and amount of specific CaS, CA, and TiN compounds that make up these complex inclusions. In many cases, the steelmaking oxides and sulfides provided heterogeneous nucleation sites for titanium nitride precipitation. This application note highlights how the combination of Perception and ChemiPhase Software on the Axia ChemiSEM System enables the detailed analysis necessary for clean steel applications.

Introduction to the Axia ChemiSEM System and Perception Software.

Duration 12:26

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