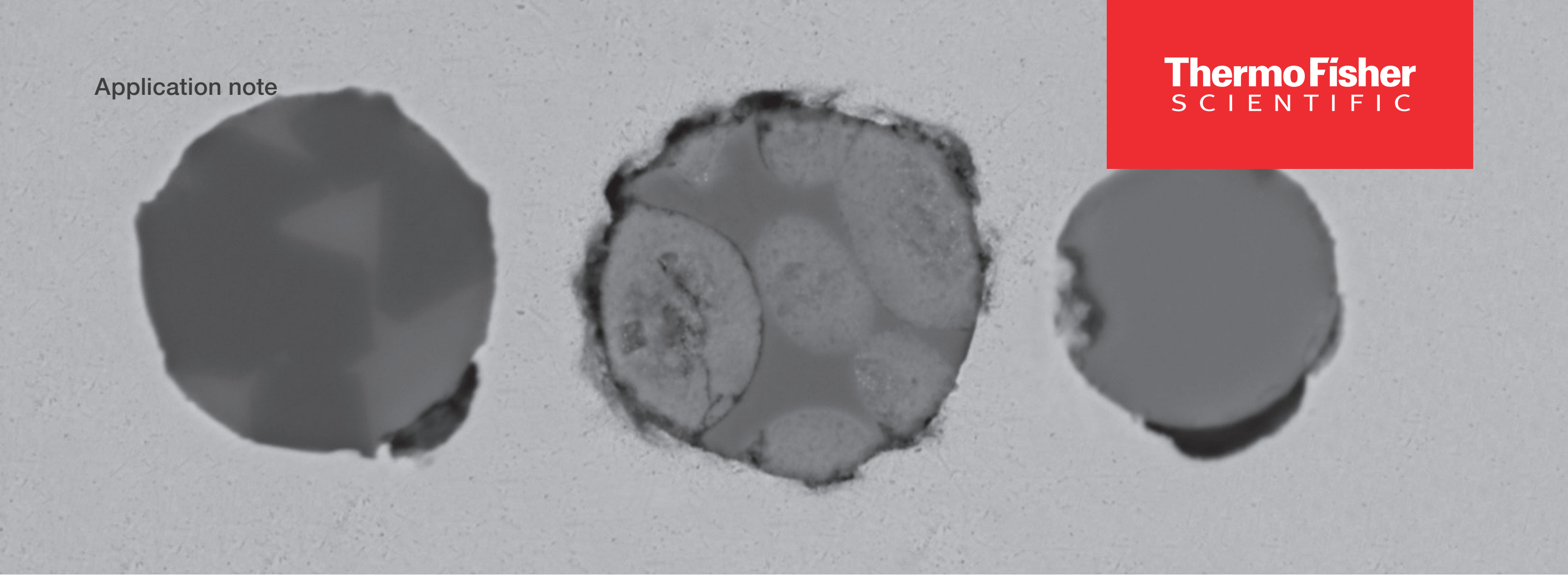
Application note



Inclusion analysis of aluminum-killed and calcium-treated steels

Liquid metal processing samples evaluated with automated scanning electron microscopy (SEM)

Introduction

Raw steel production incorporates highly oxidizing conditions into an already hot environment. Whether through the integrated blast furnace / basic oxygen furnace route or through the re-melting of scrap and alternative iron units in the electric arc furnace, the liquid steel will absorb hundreds or even a thousand ppm of dissolved oxygen. In order to reduce the activity of oxygen in the molten steel, several elements, such as carbon, manganese, silicon, aluminum, titanium, and calcium, each with a different affinity for oxygen, may be added. For example, around 200 ppm of aluminum added in the bath can decrease dissolved oxygen to about 3 ppm, resulting in micron-sized Al_2O_3 particles being distributed throughout. Alternatively, calcium has an even greater affinity for oxygen, but due to its low boiling point, it is not used for primary deoxidation but rather modification of inclusions.

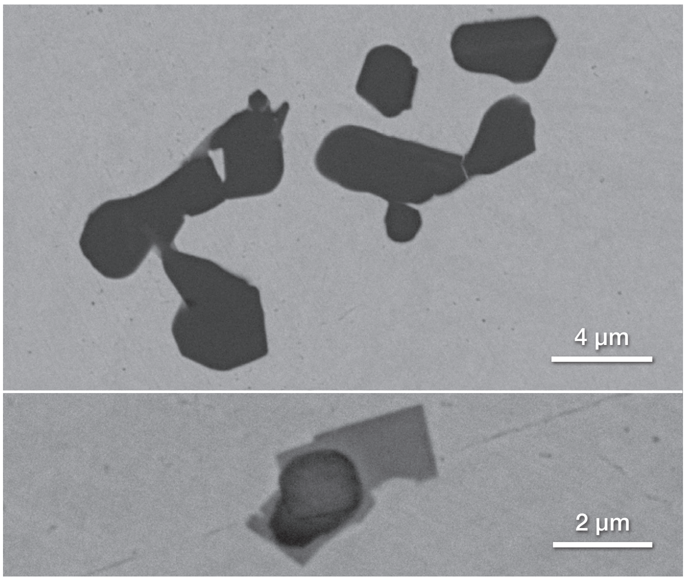


Figure 1. Manual SEM imaging of an alumina cluster (top) and TiN cubes precipitating on top of an inclusion (bottom).

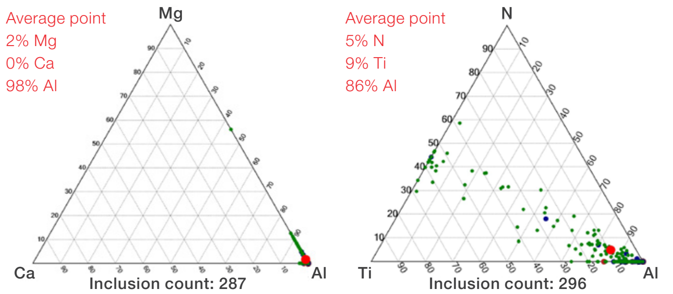
Methods and results

This study aims to show how inclusion populations change with additions of aluminum as the primary deoxidizer, titanium for scavenging nitrogen, and finally calcium modification of inclusions. The investigations shown have been made using the Thermo Scientific™ Phenom ParticleX™ Steel Desktop SEM. The backscatter detector inside the SEM easily reveals the inclusion size and shape, as they appear darker than the bulk metal. Aluminum deoxidation may yield individual inclusions generally less than 10 microns in size or clusters of inclusions that are much larger and thus have a negative impact on surface quality or fatigue life. When titanium is added, it is most often found as titanium nitride cubes, thus preventing elemental nitrogen from participating in the metal structure. Figure 1 shows a cluster of Al_2O_3 particles and a precipitate of TiN on top of an existing oxide from a mechanically polished sample of steel.

Inclusions can also be automatically characterized by the Phenom™ ParticleX Desktop SEM. The system scanned these aluminum-killed steel samples over a 60 mm^2 area for any feature over 2 microns in diameter, which in this case took about 20 minutes. At the same time, energy dispersive spectroscopy (EDS) was collected for each inclusion, which could then be classified by its composition or shape.

As shown in the Ca-Al-Mg ternary diagram of Figure 2, the oxides are nearly pure alumina, with an additional 2% Mg and 0% Ca. Because this steel was refined in the RH degasser, very little slag was entrained, and thus there is almost no contamination of the inclusions.

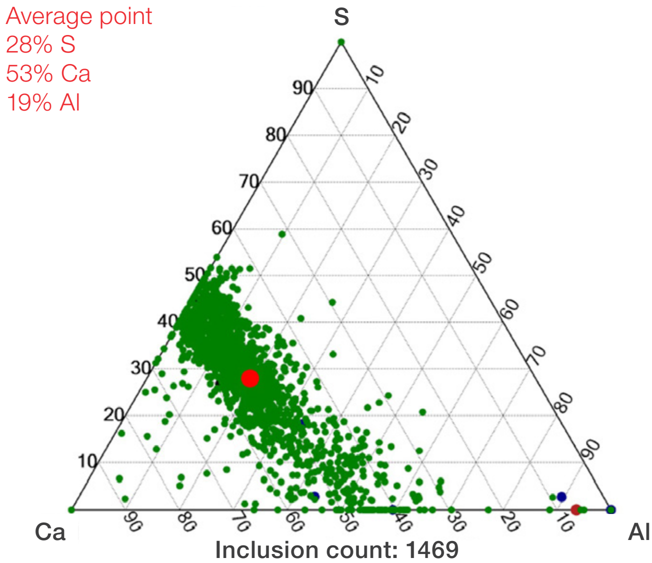
Additionally, a Ti-Al-N ternary diagram is shown in Figure 2 to reflect the titanium addition. Between the vertices of Ti and N, there is a population of pure TiN inclusions. From here to the Al corner, there is a continuum of particles where we can infer that the relative amount of Al_2O_3 in each particle increases and the TiN decreases toward the corner. The inclusion index, or area fraction percent, of alumina-type features was 0.0024%. Those Al_2O_3 inclusions are what will need to be transformed should calcium additions be added to the melt.



Classification	Particles	[%]	N	Mg	Al	Si	S	Ca	Ti	Mn	Features/mm2	Area%*	Incl.Index**
Alumina	212	71.6	1.2	0.4	92.7	0.1	0.6	0.1	4.1	0.5	3.5	83.8	0.00245
Low Mg Spinel	52	17.6	2.5	5.6	83.6		0.5		7.5	0.2	0.9	11.2	0.00033
Ti Nitride	27	9.1	37.2	0.2	10.1	0.1	1.9		49.5	0.3	0.4	4.1	0.00012
Spinel Rich	5	1.7	6.8	8.1	63.0	0.2	3.8		16.3	1.7	0.1	0.9	0.00003

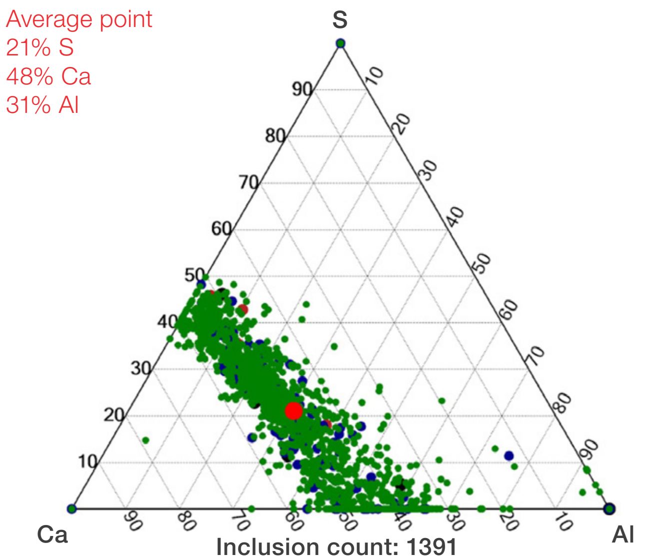
Figure 2. Automated SEM imaging of an aluminum-killed, titanium-treated steel. Ternaries of Ca-Al-Mg (left) and Ti-Al-N (right), along with particle classification table (bottom), are shown for a single sample.

Calcium-treated steels, on the other hand, produce an entirely new set of inclusions. They can further decrease the dissolved oxygen to around 1 ppm, while simultaneously modifying the existing oxides and reacting with elemental sulfur. One common purpose of calcium treatment is to modify the shape from solid oxides, which can agglomerate to low-melting-point calcium aluminates. Forming the targeted $12CaO.7Al_2O_3$ (C12A7) inclusion composition, which has the lowest melting point, requires balancing the amount of calcium added with the amount of inclusions present in the molten steel. If too little calcium is added, the inclusions will still have a high melting point and tend to agglomerate and clog the casting nozzle. If too much calcium is used, the oxides may become rich in CaO, and a new population of calcium sulfides (CaS) may form. The latter is perfectly desirable for pipe grades, which try to minimize manganese sulfide inclusions, but it is detrimental to the continuous casting refractory in the ladle or tundish that controls the flow of steel. When CaS inclusions encounter oxide refractories like ladle plates or tundish stopper rods, sulfur is released from the inclusions and the refractories are attacked by elemental calcium.



Classification	Particles	[%]	N	Mg	Al	Si	S	Ca	Ti	Mn	Features/mm2	Area%*	Incl.Index**
CaS	876	56.2	0.2	1.5	8.7	0.1	31.1	47.6	7.8	1.6	14.5	46.5	0.00830
C3A	160	10.3	0.3	4.1	27.3	0.1	12.7	43.7	9.9	1.4	2.7	7.1	0.00126
C12A7	156	10.0		5.3	37.4	0.4	5.9	35.5	12.0	2.5	2.6	6.4	0.00115
Ca Rich	116	7.4	0.9	3.2	18.8	0.1	16.4	50.5	8.4	1.1	1.9	12.6	0.00225

Figure 3. Automated SEM imaging of an aluminum-killed steel ladle sample after calcium addition. The Ca-Al-S ternary diagram (top) and classification table (bottom) show how the inclusions in this heat are very rich in calcium and sulfur, where the average inclusion has more sulfur (28%) than aluminum (19%).



Classification	Particles	[%]	N	Mg	Al	Si	S	Ca	Ti	Mn	Features/mm2	Area%*	Incl.Index**
CaS	455	30.0		1.3	11.3	0.1	33.2	50.4	1.7	1.2	7.5	15.9	0.00746
C12A7	328	21.6		5.4	42.5	0.2	6.3	39.9	4.0	1.3	5.4	60.4	0.02829
CaS Aluminate	209	13.8		2.4	24.1	0.1	23.7	46.5	2.0	0.9	3.5	9.1	0.00428
Ti Nitride	193	12.7	39.1	1.2	2.5		0.1	0.1	55.0	0.6	3.2	2.5	0.00118

Figure 4. Automated SEM imaging of an aluminum-killed, calcium-treated steel tundish sample. The Ca-Al-S ternary diagram (top) and classification table (bottom) show how the inclusions in this heat picked up aluminum and lost elemental sulfur compared to the ladle sample in Figure 3.

Figure 3 and 4 show a pair of samples taken from an aluminum-killed, calcium-treated grade, where the duration of analysis was less than 40 minutes each. One sample was taken in the ladle after all treatments were completed, and the second sample was taken in the continuous caster tundish in the middle of the heat. Though these are from the same steel, there are changes in the inclusion population that can be observed. Both the ladle and tundish inclusion types range from CaS to C12A7 and other calcium aluminates, but subtle differences may be noted. The average sulfur content in the ladle and tundish inclusions was 28% and 21%, respectively. This means that the process of transferring the steel from ladle to tundish permitted the loss of sulfur or CaS in the inclusions. To balance the loss of sulfur, there is a corresponding pickup of aluminum (as Al_2O_3) in the inclusions. The classified inclusions reinforce this concept, as the number of CaS features was halved and the number of C12A7 features doubled. In a sense, there will always be reoxidation in the tundish, so the buffer of some CaS inclusions in the ladle will help to maintain the desired C12A7 inclusion type in the tundish. In this example, the inclusion index for C12A7 type features increased from 0.0011% in the ladle to 0.0282% in the tundish. Similar comparisons could be made for any inclusion type.

The Perception Reporter software on the Phenom ParticleX Steel Desktop SEM allows the creation of unique reports with ease. With a few clicks, you can create a new template with inclusion classification tables, histograms, ternary diagrams, and more. Each section may be edited to include only the rule classes that you desire. Once a template is ready, every sample scanned can have the report automatically generated.

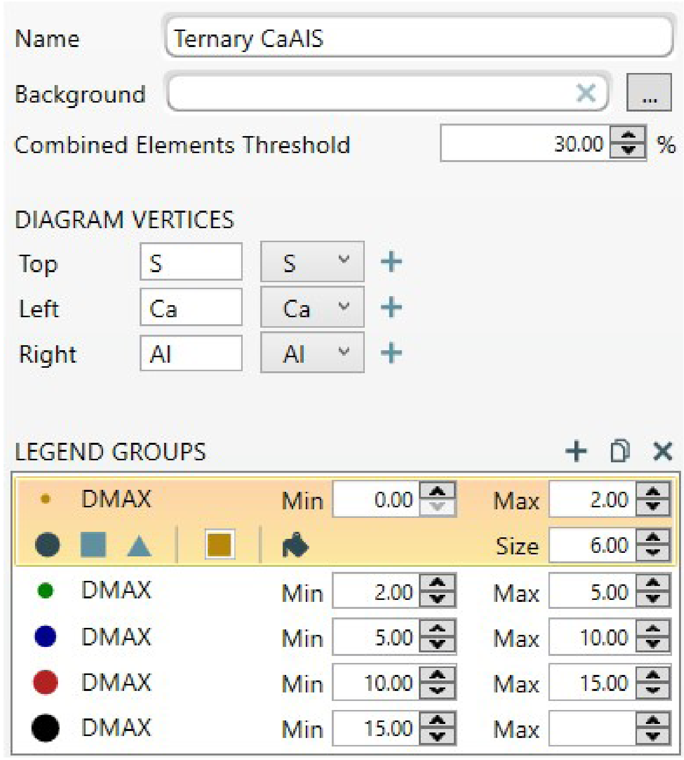
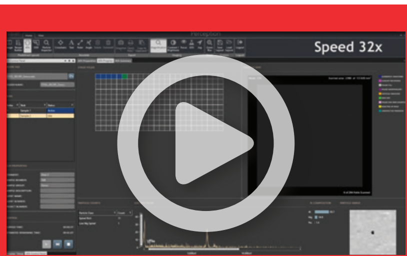


Figure 5. Snapshot of Perception Reporter shows how inclusion ternary diagrams are created with a combined element threshold, selection of up to three elements on each vertex, and editing of the spot size, shape, and color.

Conclusions

Manual and automated inclusion analysis was performed with the Phenom ParticleX Steel Desktop SEM. Primary deoxidation by aluminum and subsequent addition of titanium was shown to produce Al_2O_3-rich oxides, which were often sites for heterogeneous precipitation of TiN. Alternatively, calcium treatment was shown to produce distributions of CaS and calcium aluminate inclusions instead. Whether you are investigating new refining techniques or evaluating tundish transfer practices, rapid inclusion analysis is the key to validating the process improvement.



Phenom ParticleX Steel workflow introduction

Duration 6:23

Learn more at **thermofisher.com/phenom-particlex-steel**