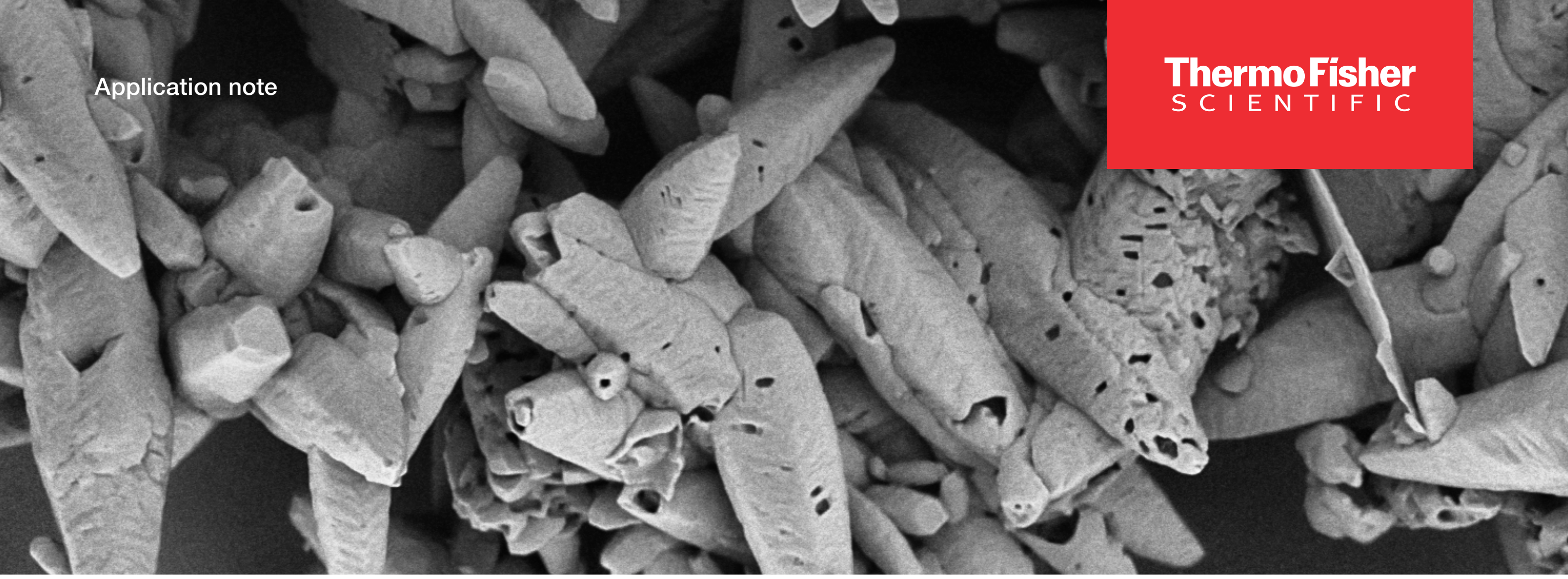

Application note

Thermo Fisher SCIENTIFIC

Benefits of low-keV imaging on beam-sensitive materials

Apreo 2 SEM imaging of calcium carbonate ($CaCO_3$) particles

Calcium carbonate ($CaCO_3$) is an important inorganic material, and it is a key mineral both in fundamental research and industry for being chemically inert. For this reason, $CaCO_3$ is generally dispersed in variable quantities (depending on the application) into other materials' matrices to change and improve their chemical or physical characteristics.

Figure 1. $CaCo_3$ applications.

Being biocompatible, non-toxic, and available worldwide makes $CaCO_3$ and related calcium carbonate-based composites interesting and attractive for many industrial applications. $CaCO_3$ is also widely employed as filler in plastic, rubber, coatings, and adhesive industries. In the last several years, its use in the biomedical field for drug delivery and tissue engineering has garnered positive attention. This incredible variability in the range of applications is determined by several strictly defined parameters such as size, morphology, and phase structure, among which the morphology and the $CaCO_3$ polymorph type are the most important.

For example, cubic and spherical particles are mainly used in the papermaking and coating fields, spindle-like shaped particles are more often employed in plastics and rubber, while rod-like $CaCO_3$ (because of its porosity) has shown promising applications in the biomedical field as bone repair material.

Scanning electron microscopy imaging on beam-sensitive materials

The particle's morphology, size, and surface area are of crucial importance, and researchers' investigation and characterization using scanning electron microscopy (SEM) is a critical step during the design of a new product and the assessment of its components for the desired application.

However, calcium carbonate is a non-conductive material that is known for its sensitivity to electron irradiation and beam damage, making it a potentially tricky sample for SEM imaging when considering the best parameters to use. The accelerating voltage first determines which interaction the beam will have with the sample. As a general guideline, high voltages correspond to a higher penetration beneath the surface of the sample (bigger interaction volume), while low voltages provide more surface information.

Low voltages and low beam currents are required to avoid charging artifacts and the induction of morphological changes to the sample. Low energy (keV) also provides surface-sensitive imaging and allows the user to characterize the general morphology of the particle(s) and the surface topography. One of the main benefits of low-keV imaging for secondary electrons is that lowering the voltage will give an increased ratio in the amount of signal generated at the surface (enhanced topography).

Materials and methods

This application note presents a characterization of two different polymorphs of calcium carbonate at different accelerating voltages and beam currents. The characterization has been conducted using a Thermo Scientific™ Apreo 2 scanning electron microscope (SEM). Specifically, the presented results were obtained with the T2 detector, an in-lens detector that is part of the Thermo Scientific Trinity™ Detection System. This unique detection system consists of three detectors (two in-lens and one in-column) which, together, offer detailed information on morphology, composition, surface features, and more.

The presented work demonstrates how SEM imaging (specifically the secondary electron imaging) changes with the different accelerating voltages. There is a focus on determining if there is an optimal combination of a low accelerating voltage and low beam current that would best highlight the calcium carbonate particles' characteristics, such as their surface topography, general morphology, and particle structure, while minimizing the effects of beam exposure.

Finding the optimum conditions

The samples of interest are two different polymorphs of calcium carbonate, specifically rod-like particles and spindle-like particles. Both have been prepared by dissolving the $CaCO_3$ powder in ethanol and, after 5 minutes of sonication, by drop-casting 5 µl of the prepared solution onto a previously cleaned silicon wafer and allowing it to air dry.

As a first approach, both samples have been imaged at 10 keV and 5 keV with variable beam currents from 0.1 nA and 0.4 nA. Some of the results are shown in Figure 2.

High-keV secondary electron imaging at low to moderate magnifications appears to make macroscopic-scale surface contrast disappear. A relatively high accelerating voltage, in fact, makes the interaction volume bigger both in X and Y directions; hence, the signal comes from a large depth and width within the sample.

As a result, at higher magnifications, micrometer- to nanometer-scale surface contrast disappears or appears translucent, and edges appear washed out (edge effect). Both effects are visible in Figure 2, especially in the images acquired with 10 keV, where the topography inside the particles is almost invisible.

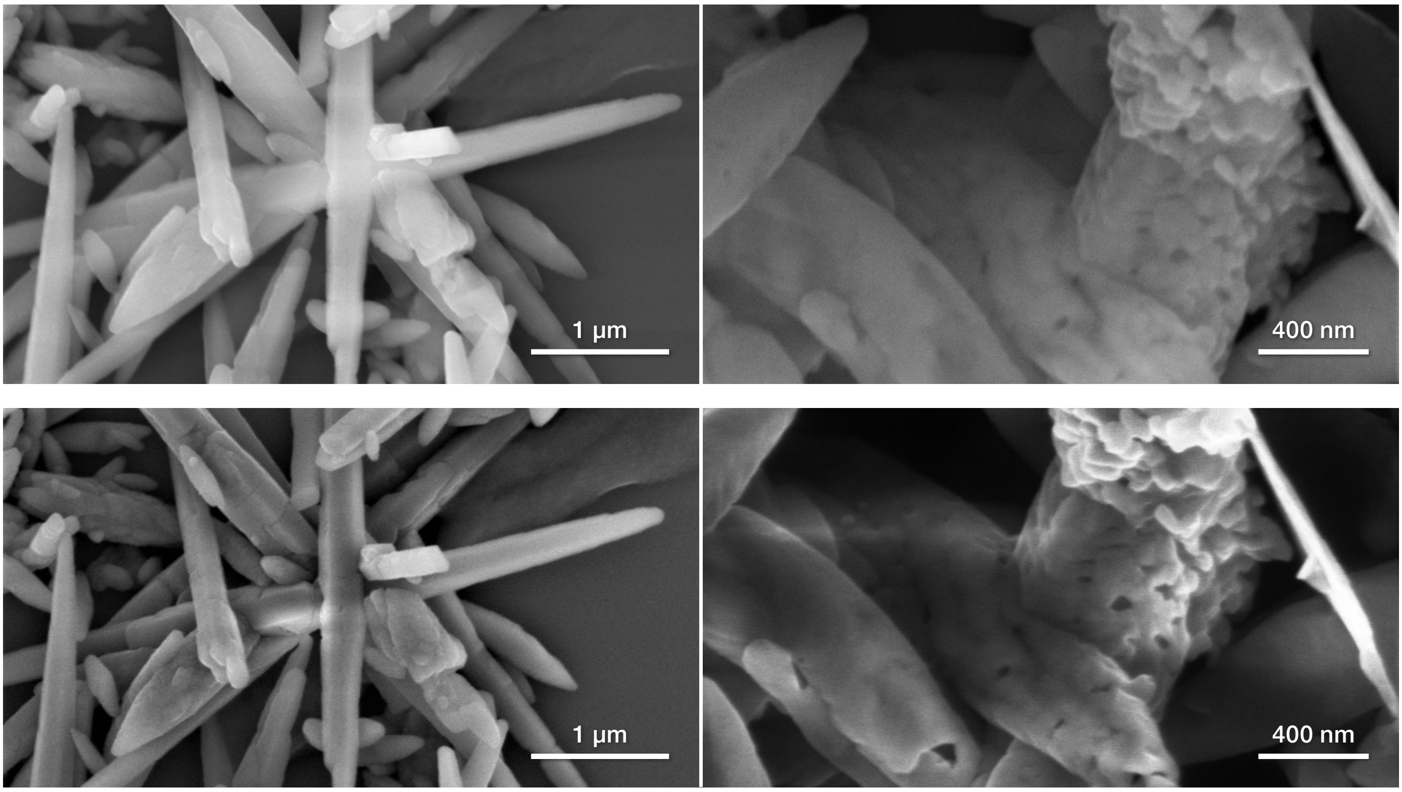

Figure 2. Rod-like $CaCO_3$ (left) and spindle-like $CaCO_3$ (right). Secondary electron images acquired with T2 detector at 10 keV (top row) and at 5 keV (bottom row).

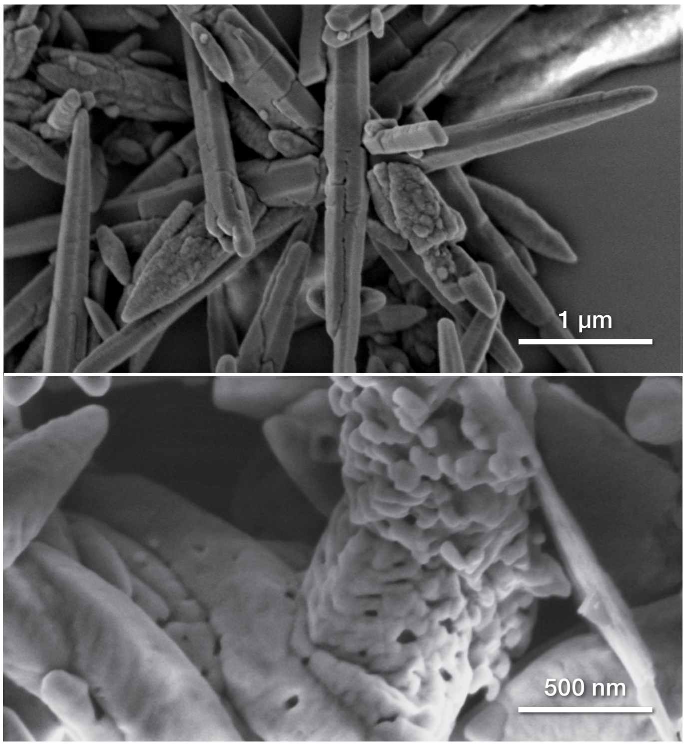

Figure 3. Same areas of the previous image from both $CaCO_3$ polymorphs acquired at 2 keV but with decreasing beam current (from top to bottom 0.1 nA, 25 pA).

Figure 3 shows the results obtained from the same areas of interest from both samples when using a lower accelerating voltage (2 keV). The morphological details provided at 2 keV are much more visible than those previously shown at 5 keV and 10 keV. Additionally, it can be noticed that further lowering the beam current helps improve the image quality (in Figure 3, the right image has been acquired with a beam current of 25 pA, while the top image was acquired with 0.1 nA).

However, to fully eliminate the charging effects visible in Figure 3 (white stripes and areas present in both images) and to reach the desired level of topographic details inside the particles (such as roughness, presence of pores, and surface morphology), both acceleration voltage and beam current have been further lowered.

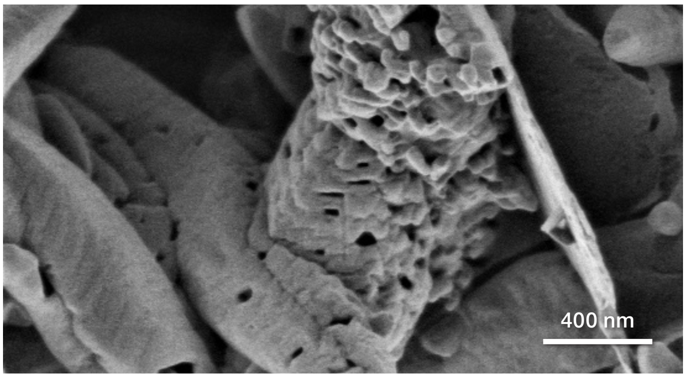

Figure 4. Secondary electron image acquired with T2 detector with an accelerating voltage of 500 V and a beam current of 6.3 pA.

Figure 4 shows the result obtained with an accelerating voltage of 500 V and a beam current of 6.3 pA. Any edge effect and charge artifacts have been removed. Moreover, there is a noticeable increase in the surface topography, as both the roughness of the particle and the presence of pores are now much more visible than at higher accelerating voltages. Pores with a diameter of about 15–20 nm have been easily measured, allowing the user a complete characterization of the particles' nanostructural information.

Hence, working with low accelerating voltages and low beam currents does not only help in reducing the beam damage or the presence of artifacts, it allows the operator to load the sample with very little-to-no sample preparation and achieve outstanding results with minimal effort.

Conclusion

Calcium carbonate is a widely used raw material in many applications. It comes in several forms and polymorphs, and some of its characteristics, such as size and shape, general morphology, and surface topography, are key in determining the specific application. For this reason, being able to achieve a complete characterization of such properties in an easy way and with fast time to results is crucial to many product manufacturers.

In this application note, the benefit of the use of very low beam voltage when studying a beam-sensitive sample such as calcium carbonate was demonstrated. High-energy secondary electrons (SE) collected by the T2 detector provide morphological information, which is enhanced by the reduced interaction volume. In addition, insulating samples in particular benefit from T2 SE detection, as these electrons are less sensitive to charging artifacts.

The image quality and resolution remain at a level where the operator can easily image such a beam-sensitive material with no risk of altering the topography and the surface structure. The Apreo 2 SEM, with its remarkable low-voltage performance, allows users to image a wide variety of samples at the appropriate conditions with minimal effort while retaining all the benefits of conventional SEM in speed, flexibility, and ease of use.

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