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Applications of Focused Ion Beam Systems in Gunshot Residue Investigation

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ABSTRACT: Scanning ion microscopy technology has opened a new door to forensic scientists, allowing the GSR investigator to see inside a particle's core. Using a focused ion beam, particles can be cross-sectioned, revealing interior morphology and character that can be utilized for identification of the ammunition manufacturer.

KEYWORDS: forensic science criminalistics, gunshot residue, focused ion beam, morphology, cross section

Scanning electron microscopy (SEM) is a well-established technique in forensic science, particularly in gunshot residue (GSR) investigations (1,2). With current techniques, however, only the surface region of a particle can be examined, so the possibility to extract more information from a particle's core exists. This has been overcome by recent developments in focused ion beam (FIB) milling technology. In the past few years, FIB systems have become widely used in the semiconductor industry, primarily in the fields of failure analysis and modification of semiconductor devices (3). This paper demonstrates that FIB also opens many new avenues of investigation of GSR particles. This is of particular interest when GSR that results from the firing of ammunition with lead-free or nontoxic primer particles is investigated, where the differentiation from environmental particles is sometimes problematic and therefore the internal morphology of particles possibly becomes an important criterion for the confirmation of the particle to be GSR.

SEM and scanning ion microscopy (SIM) are identical in principle because both use charged-particle beams scanned over solid samples to produce high-resolution images ($<$10 nm). But instead of electrons in the case of SEM, SIM uses a focused ion beam (FIB) of gallium with energies of 20 to 30 keV. A great advantage of SIM imaging is that it allows high lateral resolution without any preparation with coatings. Figures 1 and 2 show exemplar ion induced secondary electron images of GSR particles from two different kinds of lead-free ammunition. For cutting with the ion beam, a current of about 2 nA is used. The beam diameter during the cutting process is about 1 μm. The total ion dose per area for the cutting process is 20 nC/μm^2. Approximately 10 min is needed per cross-sectioning procedure. Imaging is done with a beam current of about 4 pA, which corresponds to a beam diameter of less than 10 nm.

FIB allows the examiner to cut a preselected GSR particle so that the core may be viewed. This procedure has revealed that the *morphology* of such particles on the inside is very informative with regard to the source of manufacture and therefore to the composition, even before an elemetal analysis can be done by SEM/EDX. For this study, four unique types of 9mm parabellum ammunition were used as sources of GSR particles.

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Sample Preparation

Sample particles for each of the four ammunition types were obtained by exposing four separate, typical, collection stubs to the down-range environment of the 9mm pistol. Representative particles were elementally analyzed by SEM/EDX and their locations recorded for future examination by FIB.

GECO Sinoxid™ represents a currently common ammunition with lead, barium, and antimony as the major components in the priming mixture (4). The other three represent the coming (and present) generation of environmentally friendly ammunition. These types of ammunition are designed to reduce the amount of toxic elements to which shooting range personnel are exposed in the course of their duties. EDX measurements show that GSR particles from *GECO Sintox*™ ammunition contain tin and zinc (5). Another type of ammunition, which is currently not on the market, typically has manganese and potassium in its composition. At the request of the manufacturer, this article will refer to this ammunition as '*X Lead Free*'. *Hirtenberger Lead Free*™ particles examined with EDX prove to contain strontium as detected in CCI Blaser® lead-free ammunition, too (6). Table 1 presents the major elemental components of GSR particles for the four examined types of ammunition.

Representative particles of each of these four types were then cross-sectioned with the FIB system. This was executed by scanning the ion beam over the target area. Faster scans farther away from the particle remove less material than slower scans leading up to and over the particle. This creates an etched area that deepens as it approaches the particle (see Fig. 3). Ion sputtering is then employed to ''polish'' the cross sections. The core of the particle was then examined using a line of sight along an axis parallel to the bottom of the etched region.

Results and Discussion

Figures 4–7 show examples of cross sections of the four types of GSR particles obtained with the FIB system.

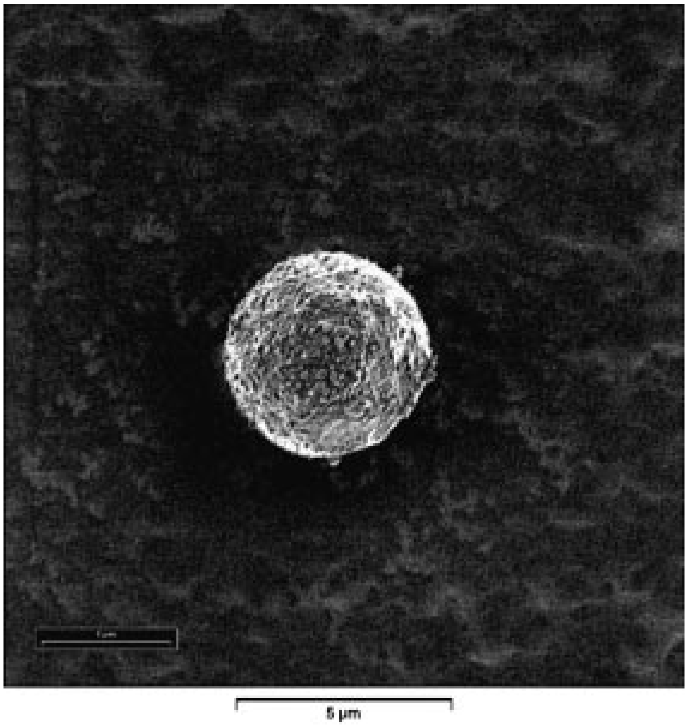

FIG. 1—*Ion induced secondary electron image of a Hirtenberger Lead Free™ GSR particle.*

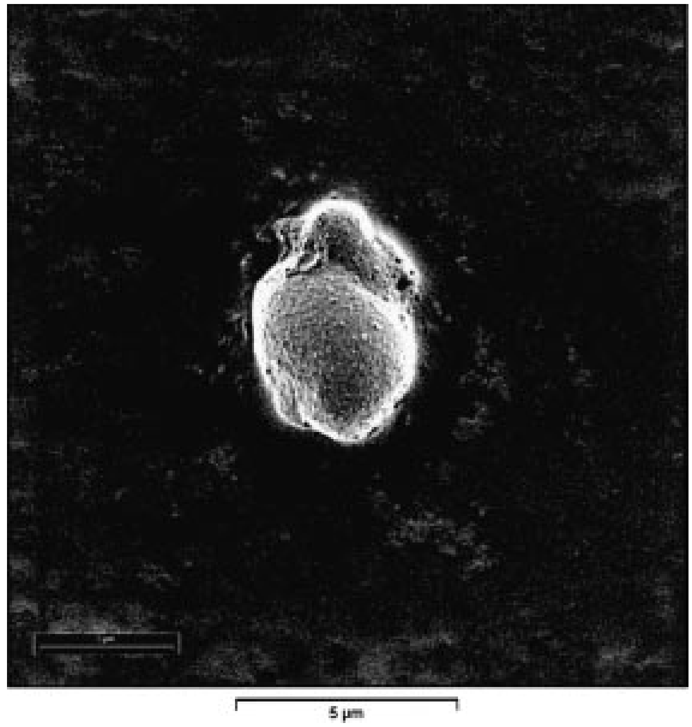

FIG. 2—*Ion induced secondary electron image of a GECO Sintox™ GSR particle.*

TABLE 1—*Major components of examined types of ammunition.*

Ammunition Type	Characteristic GSR Elements
GECO Sinoxid™	Pb, Sb, Ba
GECO Sintox™	Ti, Zn
'*X Lead Free*'	Mn, K
Hirtenberger Lead Free™	Sr

The morphological characteristics of GSR particles originating from *GECO Sinoxid™* ammunition include regular, spherical cavities (1 to 2 μm in diameter), and round lead-rich inclosures (Ø 0.1 to 1 μm). Occasionally, the interior borders of the cavities have a slightly orange-peel effect, but in general, these interior borders are unusually smooth.

The interior of GSR particles from *GECO Sintox™* ammunition also contains open or empty spaces, but they are not spherical (Fig. 5 and also Fig. 3). The interior surfaces of these particles show irregular, spongelike formations.

Unlike the *GECO* particles, '*X Lead Free*' particles are mostly solid on the inside. Cross sections show the visible internal structures comparable to winding canyons across the flat face of the cut.

Figure 7 shows a typical cross section of a *Hirtenberger Lead Free™* particle. Like '*X Lead Free*', these particles are mostly solid on the interior, with the exception of very small elliptical cavities (Ø 0.5 μm). The major unique feature of Hirtenberger particles is that they have a distinct shell on their outer surfaces. Figure 7 shows clearly that the composition of the surface is different from that of the core; however, with available analytical methods it was not possible to determine what elements were present in this shell.

After the particles had been cross-sectioned, SEM/EDX analysis was carried out on the interior of the particles, but with only partial success. As an example, the backscattered electron (BSE) image of a *GECO Sinoxid™* particle (Fig. 8) and the lead mapping results of the same particle (Fig. 9) are presented.

The smaller, bright areas of lead that are clearly visible in the BSE image are not resolved in the lead mapping image due to the information penetration depth of EDX analysis. X-rays produced by electron bombardment typically originate from an excitation volume that can extend up to 2 μm deep. Therefore, these smaller areas are only a small percentage of the measurement volume, and are not observed.

Figure 10 shows another *GECO Sinoxid™* particle that has been sectioned on both sides, and is only about 200 nm thick. The BSE image of this particle (Fig. 11) does show differences between materials, but EDX mapping is not sensitive enough to resolve the smaller zones. In order to obtain elemental information from the core of a particle, a more surface-sensitive analytical method such as Secondary Ion Mass Spectroscopy (SIMS) or Scanning Auger Microscopy (SAM) would be needed, but such methods were unavailable for this study. Such a method could be used to investigate the makeup of shell surrounding *Hirtenberger Lead Free™* GSR particles.

For further investigations, a combination of FIB with an analytical tool such as SIMS (Secondary Ion Mass Spectrometry) (7) or SAM (Scanning Auger Microprobe) in one platform would be desirable because it would allow *in situ* preparation and analysis

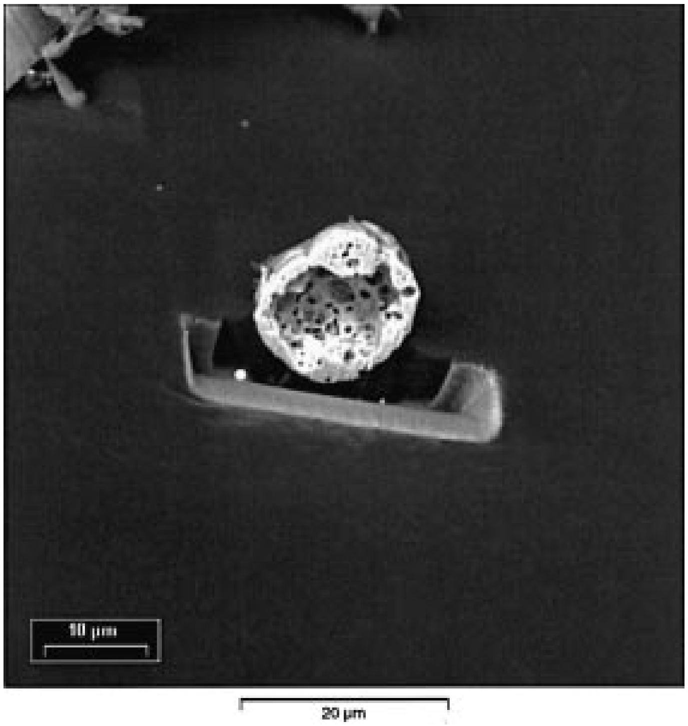

FIG. 3—*Cross section of a GECO Sintox™ particle.*

of samples. This would be beneficial for immediate qualitative data collection and better investigation performance.

Conclusions

It is important to note that some particles of all brands were solid on the inside, and therefore the interior morphology was *not* present in all of the particles sampled. However, when morphology was present, the descriptions above applied consistently and without exception to the particles from that manufacturer.

It should be recognized that this study examined a universe of only four ammunition types, and in no way suggests that each type of ammunition will have distinguishable or identifiable traits with FIB cross-sectioning. The study does show, however, that these four types of ammunition produce GSR particles with individual and unique interior morphologies.

Other applications of FIB systems in forensic science, such as the investigation of automotive paints, fibers and toner particles, are in preparation.

Acknowledgments

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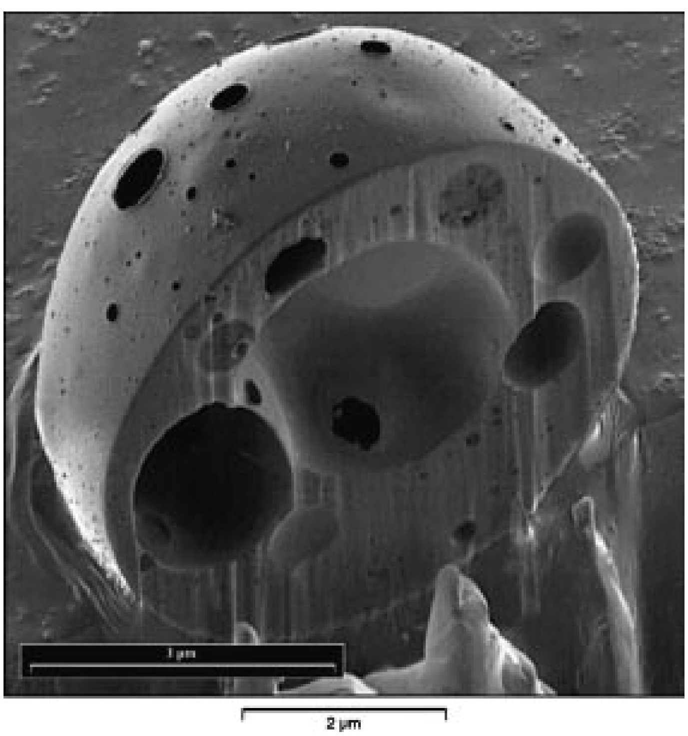

FIG. 4—*Ion induced secondary electron image of a cross-sectioned GECO Sinoxid™ particle.*

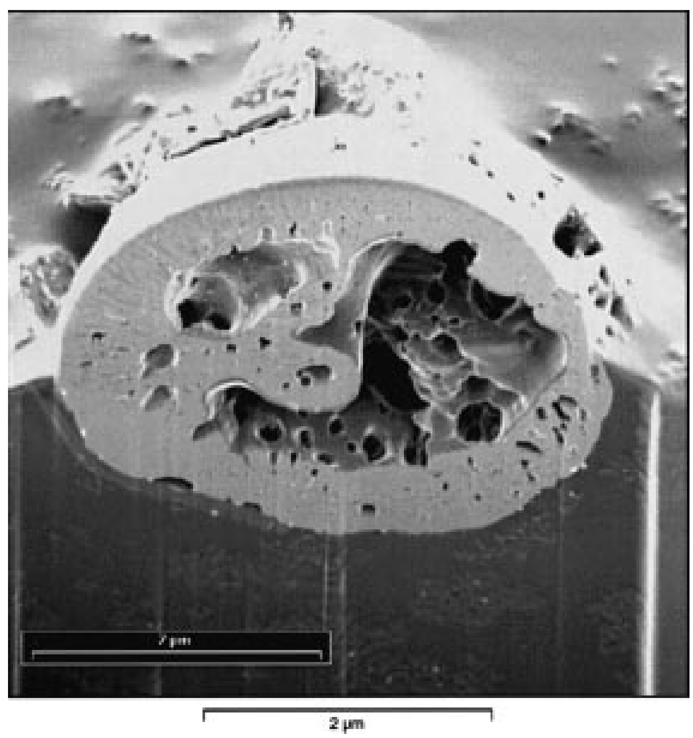

FIG. 5—*Ion induced secondary electron image of a cross-sectioned GECO Sintox™ particle.*

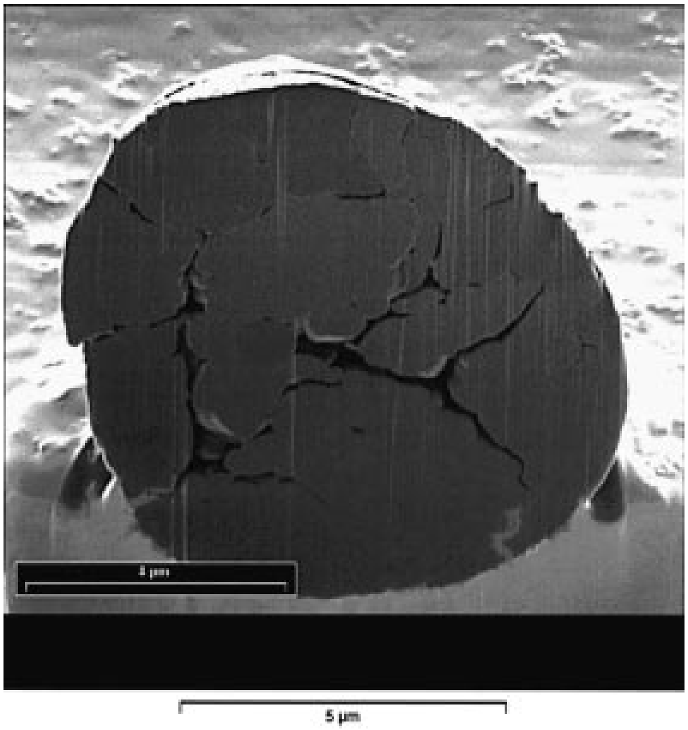

FIG. 6—*Ion induced secondary electron image of a cross-sectioned 'X Lead Free' particle.*

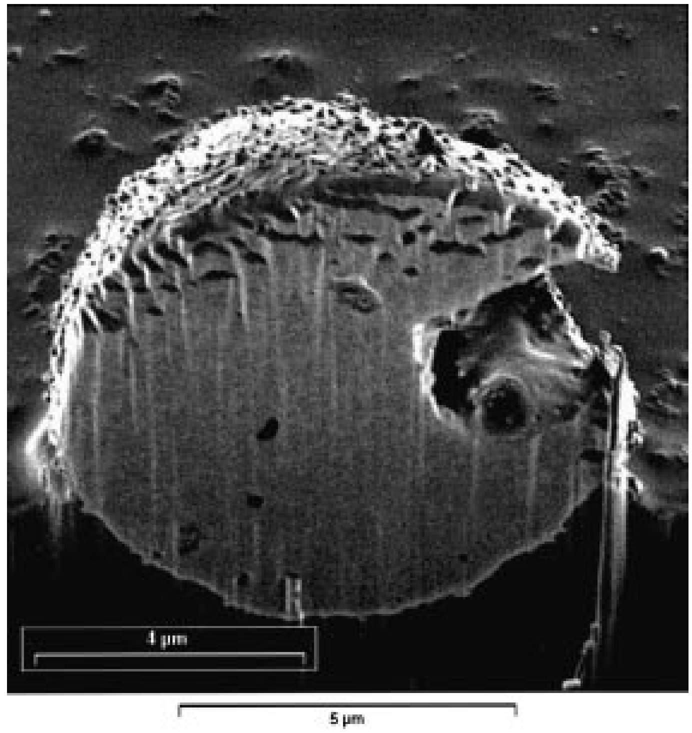

FIG. 7—*Ion induced secondary electron image of a cross-sectioned Hirtenberger Lead Free™ particle.*

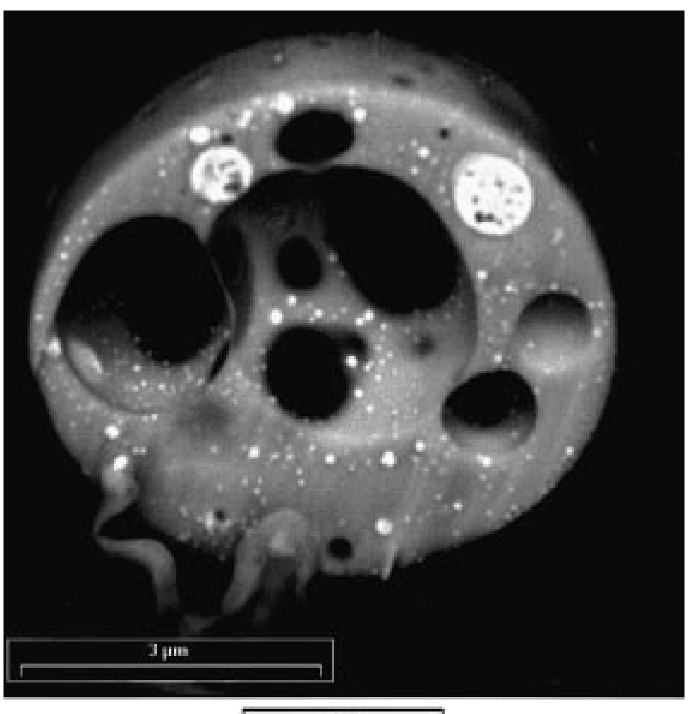

FIG. 8—*Backscattered electron image of a cross-sectioned GECO Sinoxid™ particle (see also Fig. 4).*

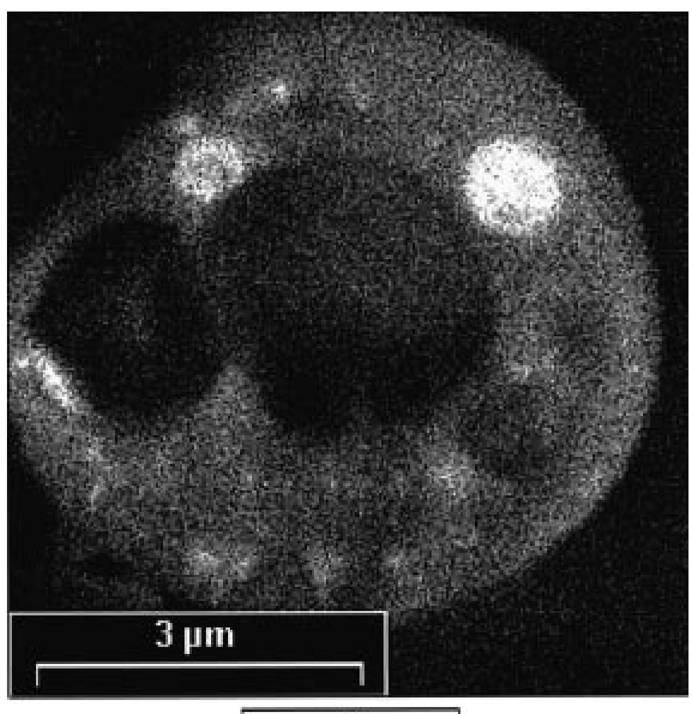

FIG. 9—*EDX Pb-map of a cross-sectioned GECO Sinoxid™ particle (see also Fig. 4).*

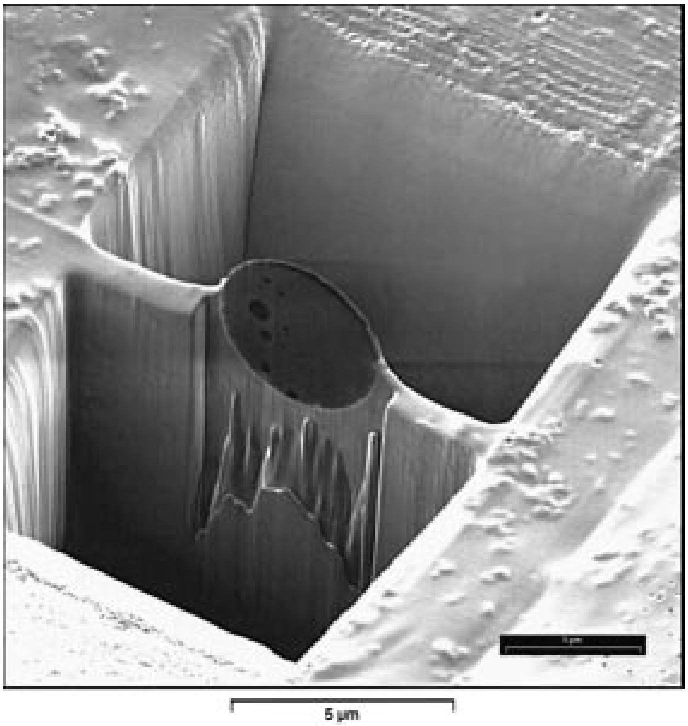

FIG. 10—*Ion induced secondary electron image of a GECO Sinoxid™ particle, prepared as a slice.*

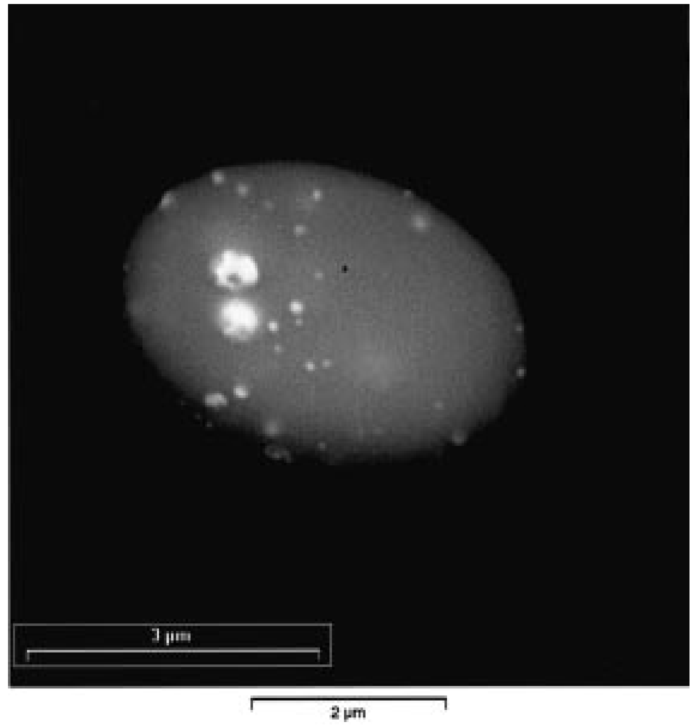

FIG. 11—*Backscattered electron image of a GECO Sinoxid™ particle, prepared as a slice (see also Fig. 10).*

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