Transmission Electron Microscopy (TEM) investigations of ancient Egyptian cosmetic powders

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ABSTRACT The processing technologies available during the time of ancient Egypt are of present concern to the field of Archaeology and Egyptology. Materials characterization is the best tool for establishing the processing history of archaeological objects. In this study, transmission electron microscopy (TEM) is used, in addition to other techniques, for phase identification and study of the microstructure and characteristic defect structures in ancient Egyptian cosmetic powders. These powders generally consist of a mix of Pb-containing mineral phases: galena (PbS), cerussite (PbCO₃), and phosgenite (Pb₂Cl₂CO₃), among others. Modern materials are fabricated according to recipes found in ancient texts to mimic the processing of ancient times and to compare with the archaeological specimens. In particular, a comparison between the dislocation structures of PbS crystals deformed in the laboratory and PbS from archaeological specimens from the collections of the Louvre Museum is presented.

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1 Introduction

Galena (PbS) is the prevalent compound in most eye cosmetics of ancient Egypt dating later than approximately 3000 BC. It is still used as a component in eye liner from Northern Africa and the Middle East. Therefore, much effort has been focused on the study of galena powders in relation to ancient cosmetics [1–4]. In addition to black galena, these cosmetics contain various amounts of white lead compounds in order to modify the shade (cerussite PbCO₃) and to protect the eye from infection (laurionite, PbOHCl, and phosgenite, Pb₂Cl₂CO₃). X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used to determine the nature and the amounts of the various components [1, 2]. In addition to these techniques, we have used transmission electron microscopy (TEM) to get a closer insight into the microstructure of the powders and relate it to the processing conditions for the manufacture of cosmetics in ancient times.

2 Experimental

2.1 Specimens

Three archaeological specimens from the collections of the Louvre Museum were investigated in this work: E23100, AF167, and MG14400a (Table 1). All specimens are Egyptian, dating from either the Middle Kingdom – from 2060 to 1786 BC (specimens E23100 and MG 14400a) – or the New Kingdom – from 1555 to 1080 BC (specimen AF167). Different aspects of these samples have been investigated previously [2, 4–6].

To shed light on the ancient processing of minerals in the production of powders for use as cosmetics, crystals of PbS were processed in the laboratory. The other compounds making up the ancient cosmetics were not included in the laboratory processing in order to focus solely on the PbS. The PbS crystals were ground in a mortar and pestle. Particles in the size range 63–125 µm were then separated by sieving. In this paper, only TEM investigations on these relatively large grains are presented. Since heating is used in the present-day production of galena-based cosmetics in northern Africa, some specimens were heated to investigate the effect of heat treatment on the defect structure. This laboratory-processed material was then compared to the archaeological specimens.

2.2 Electron microscopy

The sample preparation methods for the three archaeological specimens differed slightly due to the morphology of the powder particles. Two specimen preparation routes are presented. For the case where some of the powder particles are sufficiently thin (< 200 nm) to be electron transparent in the natural state, the particles simply need to be deposited on a grid and viewed in the TEM. For cases where the particles require thinning to achieve electron transparency, more elaborate techniques are developed.

For thin plate-shaped particles, a method has been used previously at the C2RMF in which a very small quantity of powder is dispersed in pure ethanol [7]. The powder/ethanol solution is then agitated ultrasonically until all powder is suspended (approximately 10 minutes). A pipette is then used to draw and deposit a drop of solution on a standard TEM carbon foil backed with a copper grid. The foil is then allowed to dry,
depositing powder particles on the carbon foil. The sample can then be placed directly into the microscope. This method is preferred, when applicable, due to its simplicity. Another benefit of this method is that since the particles are not altered during foil preparation there are no sample preparation artefacts as in the case with other methods. This method was used to produce TEM foils for sample MG14400a.

A more classical preparation method was used for modern samples and archaeological samples AF167 and E23100. Powders were mixed with a low temperature curing epoxy and infiltrated into copper washers with a thickness of 0.3 mm [4]. The epoxy was then allowed to cure, forming a bulk sample which could then be processed using standard TEM sample preparation techniques. The samples were then mechanically thinned to 50 microns thickness and further thinned at the center using a dimple grinder. The sample is then ion thinned to electron transparency using a Gatan™ Precision Ion Polishing System (PIPS).

There are a few features of the thinning preparation techniques which may lead to a skewing of the experimental observations for a given specimen. In the case where particles are simply suspended in solution, the process selects out particles which can form a suspension in ethanol during ultrasonic treatment. In the second case, perturbations of the microstructure may arise from temperature elevations (as high as 80–100 °C), mechanical stresses during various handlings and damage by ion bombardment. Using conditions which are adjusted to be as gentle as possible minimizes the amount of features introduced during preparation. These features, when they exist, are usually easy to identify. Finally, electrons in the microscope, as well as any other kind of beam, can be the origin of damage during the observation of unstable compounds, such as those containing water or other groups which may volatilize or otherwise degrade in the electron beam.

For the actual performance of the TEM, two microscopes were used in this work. A Philips CM20 operating at 200 keV was used for basic imaging and X-ray energy dispersive spectroscopy (XEDS) and a Jeol 200CX operating at 200 keV was used for imaging of dislocations and dislocation structures.

3 Results and discussion

3.1 Laboratory-processed powders

Material produced from hand-crushing of PbS powders have been investigated for comparison with the archaeological specimens. The dislocation structure, as seen by TEM, is dominated by straight segments along (100)-type directions with Burgers vectors of type \( a/2(110) \) at 45° to the dislocation line [4].

In addition to the straight dislocation segments, there is a significant amount of dislocation debris along longer segments. There is a high density of dislocations which turn abruptly at right-angles with reactions at the turning point. Super jogs may also be responsible for some of these right-angle features [6]. Dislocation bundles are quite often seen around long dislocation segments. These bundles are in close proximity to other dislocations, but do not interact. Loops and dipoles are also common features in the room temperature dislocation structure. These features have all been explained by considering the random application of stress which occurs during the hand grinding of powders [6]. Under the application of small deformations along random directions, dislocation glides occurs successively in all available slip planes. As dislocations glide relatively short distances in different planes, dislocations interact leaving the types of dislocation structures described earlier.

When these powders are heated to 300 °C (0.42 of the melting temperature) for 2 hours, a small amount of recovery occurs. Subboundaries form in some regions of the sample with an average inter-subboundary distance of approximately 1 \( \mu \)m. Between the subboundaries, the density of dislocations is reduced and the dislocations are rearranged. The subboundaries are formed by climb at the relatively low temperature of 300 °C [4].

3.2 Archaeological sample AF167

A first exploration was previously made on the archaeological specimen AF167 with the aim of examining the dislocation structures [4]. Although this powder contains 13% anglesite (\( \text{PbSO}_4 \)) (Table 1), this compound was not identified in the thin areas because it was either lost during foil preparation (preferential thinning) or it was overlooked perhaps due to being agglomerated with the fine particles of PbS. In order to assess the origin of anglesite in these cosmetics, more investigations are necessary.

AF167 consists mainly of large grains (50 to 100 \( \mu \)m [4]) of galena. In one such grain, a zone of about 3 \( \mu \)m was found to include small PbS grains (sizes 0.1–0.3 \( \mu \)m). These may be a pre-existing feature of the original ore used by the Egyptians for cosmetic fabrication and not the result of processing.

Dislocation structures have many similarities with those observed in powders prepared in the laboratory [4]. In some zones, many dislocations are along (100) directions with the Burgers vectors at 45° to the dislocation lines (Fig. 1a). In many cases they turn by 90° at a point with no visible reaction [6]. Dipoles are also observed. The density of dipoles is higher than in the laboratory-prepared powders (Fig. 1b). The origin of the dipoles may be either the preparation conditions in ancient times [4] or perhaps be the result of glide recovery during 3500 years at room temperature. Dislocation patterning (Fig. 1a) has also been observed with bands parallel to (010). The bands are separated by 5 \( \mu \)m zones containing a high density (5 × 10⁸ cm⁻²) of dislocations [4]. This pat-

<table>
<thead>
<tr>
<th>PbS (Galena)</th>
<th>PbCO₃ (Cerussite)</th>
<th>Pb₂Cl₂CO₃ (Phosgenite)</th>
<th>Other Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>E23100</td>
<td>58.3%</td>
<td>16.8%</td>
<td>&lt; 0.3% Anglesite (19%)</td>
</tr>
<tr>
<td>AF167</td>
<td>82%</td>
<td>–</td>
<td>Anglesite (13%)</td>
</tr>
<tr>
<td>MG14400a</td>
<td>–</td>
<td>86.6%</td>
<td>Cotunnite, Quartz</td>
</tr>
</tbody>
</table>

**TABLE 1** Mineral phase composition of the specimens examined in this work. The phase composition is determined by XRD using synchrotron radiation [2].