Use of gold/palladium surface replicas for high kV(30), SEM examination of low Z materials

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Abstract. A procedure for making high fidelity gold/palladium surface replicas of various low atomic number (Z) materials for SEM examination has been developed. The procedure facilitates simultaneous replication of a number of SEM specimens. These replicas provide improved image quality, elimination of charging and beam penetration artifacts and microtopographical information, often not available by direct SEM examination of low Z materials at 30 kV.

Keywords. Scanning electron microscopy; low Z specimens; resolution; replica; perspex; gold; palladium.

1. Introduction

Quite often, an actual specimen to be studied is not suitable for direct emissive mode examination in the SEM particularly at high kV and high magnification. For example, fragile materials such as cotton fabric and unstained or unfixed biological materials may suffer severe thermal damage due to the high energy of the beam. Besides, siliceous, amorphous and microporous materials such as diatomaceous earths, zeolites, catalysts, etc. exhibit random charging due to adsorbed water. Specimens such as skin, teeth and machine parts cannot be moved to the specimen chamber of the SEM. In such cases surface replicas of the specimens have to be made and examined in place of the actual specimens. For a given accelerating voltage, beam damage and charging are proportional to the extent to which the beam can penetrate into the bulk of the specimen. Since this range of penetration (Bethe range) varies inversely as the atomic number (Z) (Wells 1974) of the material of the specimen, the damage and charging artifacts are particularly severe with materials such as above. Besides these artifacts, the other effects of beam penetration namely obfuscation (Koch 1975) of the surface topography (i.e. the appearance of overlapping images of underlying structures of the specimen) and flaring of small structures (due to the signal emanating from their entire surface), further deteriorate the image. Although efficient coating techniques can often effectively eliminate the damage and charging artifacts, loss of resolution of fine details of low Z materials during high kV examination imposes severe restrictions on the useful magnification of the image. Although lower kV (5-10kV) reduces beam penetration, the expected benefit is often nullified at high magnifications, due to increased noise levels and electron optical aberrations associated with low kV beams.

Generally materials like 'Silflo', acetate tape, poly-ethylene, etc have been used for making the negative replica and araldite for positive transfer. However, for obtaining an impression of high Z replication material for improved image quality a novel procedure was employed using 'Perspex' for making negative imprint and Au/Pd reinforced with copper for making the positive replica. The results obtained with various materials examined directly in the SEM or after using this new replica technique are described in this paper.

2. Materials and methods

2.1 Materials

The following materials and their Au/Pd replicas were examined in the emissive mode at 30 kV in the Cambridge Stereoscan S4-10: (a) cotton fibre (b) diatomaceous earths (Kieselguhr) (c) gypsum (d) zeolite (e) nickel catalysts.

2.2 Replica making technique

One inch square sheet of 3 mm thick perspex was placed on a large SEM stub. The stub was placed over chloroform in a closed petridish which was kept warm (50°C) over a hot plate. About 1 mm thick surface layer of the perspex sheet got sufficiently softened over the chloroform vapour in an hr. The softened plastic was pressed onto the specimen mounted on a glass slide. The whole assembly was then held in a clamp which was gently tightened and kept overnight in an oven at a temperature of 60 to 70°C. When the solvent evaporated and the plastic hardened, the assembly was cooled to room temperature and the glass slide detached from the plastic negative replica. The replica was cleared of the specimen material by various processes depending upon the nature of the material. For example, (i) Cotton fabric could be pulled off with a pair of fine forceps. The remaining fibres were dissolved in cupriethylenediamine hydroxide (Cuene). (ii) Silicious materials such as Kieselguhr, rice husk silica, zeolites and catalysts were treated in hydrochloric acid and then dissolved in hydrofluoric acid.

After clearing the material, the replica was treated in a detergent solution, washed with distilled water and dried in a dessicator. (Sonication for a few seconds during cleaning also helps in dislodging small particles). The positive replica was made by plasmaglo cleaning of the negative, followed by vacuum deposition of about 2 inch length of 0.020 inch/0.5 mm diameter gold/palladium wire (60:40) onto the cleared plastic negative replica using a tungsten basket heater. The thin gold/palladium film was reinforced by vacuum deposition of copper through a molybdenum boat, followed by a sufficiently thick layer of electrodeposited copper. The copper plating bath consisted of a saturated solution of copper sulphate containing a few drops of concentrated sulphuric acid. The electrodes were made of heavy gauge copper strips. The coated negative replica was attached to the cathode with silver dag. Plating was done initially at a current of 100 mA for 30 min followed by 500 mA for 3-4 hr. By the end of this period the copper deposit was sufficiently thick to impart rigidity to the gold/palladium film.

The composite replica was detached from the electrode carefully, washed thoroughly and dried under vacuum. The plastic was dissolved in chloroform on a hot plate at

about 50°C. The metal replica was further washed in detergent solution followed by acetone and dried *in vacuo*.

For eliminating stray charging lines arising from any foreign particle still attached to the replica surface, a very thin (0.25 inch length of 0.7 mm diameter wire) layer of silver was vacuum-deposited on the replica whereas the samples examined directly were coated with 1.5 inch silver wire. All the samples and their replicas were plasmaglo cleaned prior to coating.

3. Results

3.1 Cotton fibre

Figure 1 shows an old cotton fibre examined directly in the emissive mode at 30 kV. The surface of the fibre is seen to be damaged. There is negligible charging and the bunch of fibrils of the primary wall can be discerned as the cuticle was dissipated. The fibrils appear to be heavily encrusted with soil and a clear delineation of fibrils is not possible. The same region examined at 5 kV (figure 2) shows lesser darkening of the image due to reduced beam penetration. However, increased noise level and decreased resolution have further obscured the details as seen in figure 1. Figure 3 shows the replica image of a damaged fibre. The fibrils in figure 3 are extremely well-defined (*cf.* poorer quality image seen in figure 1). Figure 4 depicts replica of a new cotton fibre with intact cuticle, indicating that replication procedure was not responsible for the appearance of the fibre in figure 3.

3.2 Diatomaceous earths

Figures 5 and 6 clearly depict the considerable improvement in image quality of fine structures provided by the replica technique. Figure 7 shows the replica image of a sample of German Kieselguhr. When the material was examined at 30 kV the plates showed porosity similar to that seen in figure 5. However, examination of the replica (figure 7) revealed that the porous appearance was a case of image obfuscation, suggesting that the diatomaceous plates of the sample consisted of a porous interior sheathed inside a nonporous, membranous wall.

3.3 Gypsum

Figure 8 shows the image of a sample of gypsum made in the laboratory. Direct examination of the material shows considerable flaring of the crystals and electron channelling contrast. The image of the replica (figure 9) showed elimination of these artifacts and facilitated a more accurate estimation of the crystal size distribution.

3.4 Zeolites

Figure 10 shows the image of a sample of zeolite and figure 11, that of the replica of the material. The improvement in image quality, even at a low magnification ($\times 700$), in the replica has clearly brought out the "potato" structure (McCrone and Delly 1973) and porosity of the zeolite particles in figure 11.

Figure 1-2. 1. Direct examination. Old, damaged cotton fibre. 30kV $\times$ 7000. 2. Direct examination. Same region of the cotton fibre at 5kV $\times$ 7000.

Figures 3-4. 3. Replica. Au/Pd. Old, damaged cotton fibre 30 kV $\times$ 7000. 4. Replica Au/Pd. New cotton fibre with intact cuticle. 30 kV $\times$ 8000.

Figures 5-6. 5. Direct examination. Kieselguhr 30 kV $\times$ 7000. 6. Replica. Au/Pd. Same sample as in figure 5 30 kV $\times$ 7000.

Figures 7-8. 7. Replica. Au/Pd. Sample of Kieselguhr showing absence of characteristic porosity 30 kV $\times$ 7000. 8. Direct examination. A sample of gypsum 30 kV $\times$ 1600.

Figures 9-10. 9. Replica. Au/Pd. Same sample of gypsum 30 kV $\times$ 1600 10. Direct examination. Zeolite sample 30 kV $\times$ 700.

Figures 11-12. Replica. Au/Pd. Zeolite sample (corresponding to figure 10). 30 kV $\times$ 700.
12. Direct examination. Nickel catalyst showing the structure of the silica support 30 kV $\times$ 7000.

Figure 13. Replica. Au/Pd. Nickel catalyst. 30 kV $\times$ 7000.

3.5 *Nickel catalyst*

Figure 12 shows the topography of a sample of supported nickel catalyst. When a replica of this material was examined (figure 13), an entirely different topography was seen. Thus figure 12 is a case of beam penetration artifact (obfuscation) and depicts the particulate structure of the support material since the overlying nickel deposit was thin enough to be electron transparent at 30 kV. The gold/palladium replica of the nickel deposit being electron opaque has clearly delineated the topography of nickel in figure 13.

4. Discussion

Many of the materials examined in the SEM have a nonhomogenous chemical structure. Hence the emissive mode image of a surface will simultaneously present both topographical and chemical contrast — the latter arising from the various surface components of the specimen which differ in their secondary electron emission properties. If the surface contains crystalline regions or inclusions, the image will also present electron channelling contrast along lattice defects (figure 8). Quite often chemical and channelling contrasts presented by an emissive mode image can provide some useful information independent of the topographical features of the specimen. However, in purely topographical investigations on materials, such variations of electron emissivity can lead to erroneous interpretation of SEM images.

A surface replica of an SEM specimen being of uniform composition and structure, presents only the topographical features of the surface of the specimen. The basic process

of replica making, namely transferring the specimen topography to a negative and from the negative replica to a positive is common to the replication of all kinds of materials. However, since the negative replica signifies the first stage of transfer of the impression of the specimen surface, the material for the negative replica has to be so chosen that it produces an accurate and stable impression, does not distort or chemically react with the specimen and can be easily detached from or cleared of the specimen material. The specimens examined in the present study were sufficiently rigid to withstand, without distortion, the contact pressure of softened perspex and transfer to the negatives, surface features as small as about 400 Å which value compares well with the results reported by Hearle *et al* (1974) using "formvar". Other materials such as polystyrene, celluloid and synthetic elastomers (Silflo) have also been tried by some workers with varying degrees of success. However, a disadvantage of such substances as well as perspex tried in our experiments, is that they employ nonpolar, lipidophilic solvents which may in some cases (figure 3) solubilise some components on the specimen surface such as oily soils on fabric and lipids in animal tissue and hence the use of substances such as methylated celluloses, acrylic and polyvinyl resins has been suggested by some authors. (Hearle *et al.* 1974)

Some of these low Z materials have also been used for making the positive replica. One of the earliest techniques using Silflo for the negative and araldite for the positive replica has been found to be most suitable for the replication of soft biological tissues such as the skin. However, there is some loss of detail in preparing the positive which also produces a number of artifacts, thus restricting the usefulness of the technique to low magnifications (Pameijer 1975). The Au/Pd technique allows examination of low Z materials at very high magnification without the above mentioned problems.

Although a material such as araldite has uniform electron emissive property, on account of its low Z value (like the original specimen) beam penetration artifacts are not reduced by its use. A heavy metal such as gold reduces beam penetration and hence the radial spread of secondary emission by many orders of magnitude, to give a high resolution image. Besides, vacuum-deposited metal films do not suffer from the problems of wetting and 'contact' artifacts as with the araldite procedure. Au/Pd alloy (60:40) gives extremely fine grained films. Grain growth during vacuum deposition on the inert surface of perspex is eliminated due to plasmaglo cleaning of the negative replica prior to coating. Although thicker coatings may improve the quality of replicas, the amount of Au/Pd wire used in the study gives an adequately thick electron opaque film for 30 kV examination.

The subsequent copper coating was carried out with the intention of protecting the Au/Pd film during its transfer to the copper plating bath.

If the surface of the specimen contains very minute reentrant cavities, then clearing and washing of the replica present problems. Trapped particles of the specimen material or insoluble deposits from the plating bath can give rise to fine charging lines during the examination of the replica (figures 7 and 9). Sonication for a few minutes during the detergent wash dislodges most of such deposits and does not seem to affect the replica adversely. As a further precaution against charging, the replicas were plasmaglo cleaned and coated with a very small amount (0.25 inch × 0.7 mm diameter wire) of silver.

Thus the Au/Pd replica technique gives significant improvement in topographical detail with respect to both contrast as well as resolution. An added advantage of using

a thick perspex plate is that many replications (large number of samples) could be made at a time.

5. Conclusion

The use of Au/Pd surface replicas of low Z materials gives high resolution emissive mode SEM images which present the true topographies of the original specimens. The improved image quality provides valuable information on the microtopographies of both biological and non-biological materials.

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