THE PREPARATION OF FINE PARTICULATE FOR ELECTRON MICROSCOPY INVESTIGATIONS USING DENTAL AMALGAM

L.S. CHUMBLEY, F.C. LAABS, S. C. SANDERS
Ames Laboratory, 214 Wilhelm, Ames, IA 50011

ABSTRACT

Samples of high Tc superconductors and metal powders have been prepared for Scanning and Transmission Electron Microscopy examination by a novel method. Dental amalgam, commonly used for filling cavities in teeth by dentists, has been used as a binding agent to hold the sample particulate together during sample preparation. The amalgam was pressed into a small rod 3 mm in diameter and samples were prepared by cutting slices from the rod followed by mechanical grinding and ion milling to perforation. This technique is extremely easy and offers several advantages over other preparation methods. Experiments revealed difficulties due to preferential sputtering yield, but generally these could be overcome and good thermal and electrical properties of the amalgam partially offset the former inconveniences. It should be possible to use this technique for any number of materials, including ceramic materials and small non-spherical particulate.

INTRODUCTION

The preparation of thin foils from small particulate for examination by Transmission Electron Microscopy (TEM) has always been difficult. While various plating techniques are often used, these methods are often quite involved and require a considerable effort before a TEM specimen is produced. They also may be ineffective when dealing with materials which have low electrical conductivity, such as geological samples, oxides, and ceramic compounds. These materials are often examined by simply crushing the sample and placing the resultant chips on a carbon-coated grid. While this method is easy, altering the character of the microstructure by crushing is always a possibility. Another means of examining particulate is to disperse the powder in an epoxy resin. However, most resins are insulating and electrical charging of the sample can occur when exposed to an electron beam. Many resins lack the strength necessary to withstand being thinned to < 100 μm, and considerable care must be taken during specimen preparation to avoid cracking of the sample mount. This can make the thinning process a tedious and time consuming operation.
In an attempt to avoid many of the problems listed above, experiments have been conducted using dental amalgam as a binding agent in order to examine flakes and powders of various high T_c superconductors and metals using TEM and Scanning Electron Microscopy (SEM). Dental amalgam is an alloy consisting principally of Ag and Hg. Hg exhibits extended solubility in Ag and when mixed in the proper proportions the two elements react and quickly form a solid solution which subsequently hardens at room temperature. It is ideal for use as filling material for teeth since the mixed compound remains soft for several minutes, after which it hardens into a strong, relatively inert compound. It is these same characteristics which make it an attractive choice as a mounting material for TEM samples. A detailed description of the sample preparation method follows.

EXPERIMENTAL PROCEDURE

Amalgam is categorized according to the length of time necessary for the mixture to harden. For example, a regular-set amalgam will be fully hard in 12 minutes while a fast-set will harden in 9 minutes. The amalgam used in this study was Kerr Regular Set 400mg capsules. An amalgam capsule consists of two sections; one section contains the Ag alloy powder (alloyed with Sn and Cu to determine the set) while a sealed end contains Hg, Fig. 1. When a sample, is prepared the two sections of the capsule are pulled apart and the particulate material to be examined is added to the Ag alloy powder. The ends of the capsule are then rejoined, and the amalgam capsule is processed. In this study, all of the samples were shaken by hand to mix the alloy powder with the material to be studied. Once this was done, the two ends of the capsule were forced together, breaking the sealed end and allowing the powder and Hg to mix. Trituration of the amalgam was then achieved by shaking the capsule vigorously. The length of trituration depends upon the type of shaking device used and was a critical step in determining the hardness characteristics of the amalgam [1]. In this study, two types of devices were used, namely, a Crescent 'Wiggle-Bug' Dental Amalgamator and a SPEX mill, Fig. 2. Recommended trituration times for the amalgam were from 15 - 30 seconds in the 'Wiggle-Bug', however, the resultant compound was found to be dry and crumbly which is a sign of under trituration. Since the addition of the particulate material was apparently affecting the mixing characteristics, the length of time was then increased to 120 seconds and the capsule was shaken in the SPEX mill. This process yielded much better results. After trituration the mixture was removed and pressed into a die 3 mm in diameter, figure 3, and the die was clamped between the jaws of a vise. The amalgam hardened in a matter of minutes, and the rods thus produced were removed from the die. Samples for
Figure 1. A typical amalgam capsule separated into the two separate halves. The Ag alloy powder is contained in the left half while the Hg is in a sealed reservoir in the right half. When the two halves are rejoined and then pressed together, the seal is broken and the Hg is free to mix with the Ag alloy powder.

Figure 2. Shaking devices used in this study. a) The Crescent 'Wiggle-Bug'. b) A SPEX shaker mill showing the sample in position.
Figure 3. A 3 mm TEM sample punch was used with a die to form the amalgam into 3 mm rods. The rods were sliced and dimpled with a felt covered wheel.

Figure 4. Nd$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ superconducting powder mounted for a) optical and b) SEM investigations. Ceramic powders were easily identified when mounted in the amalgam.

TEM observation were prepared from slices cut from the hardened rods using conventional mechanical thinning and dimpling followed by ion milling to perforation. Both Gatan and Ion Tech ion millers utilizing LN$_2$ cold stages were used for this study. The milling conditions used varied depending upon the sample and the miller used. Since the milling rate of the amalgam depends upon the set chosen and the amount of trituration, care must be taken during this step. In general, the amalgam was found to mill faster than all of the samples examined, the difference being more pronounced for the ceramic samples. This difference in milling characteristics was the major problem associated with this technique, however, it should be noted that thinning problems due to different milling rates is also common to mounting techniques involving resins and epoxies.
EXPERIMENTAL RESULTS

Ceramic Samples

A micrograph of a section polished for optical and SEM examinations of Nd1Ba2Cu3O7-δ high temperature superconductor powders is shown in Figure 4. In general, the amalgam bonded well to these materials and offered good edge retention when polishing cross sections. The strength of the amalgam prevented smearing of the mount over the surface of the powders when polishing, and its conductive nature eliminated the need for C or Au coating before SEM investigations. In a similar study, a TEM sample was prepared of blown fibers of the superconducting compound Bi2Sr2CaCu2OX. A low magnification optical micrograph of a TEM sample prepared of a small flake is shown in Figure 5a. A hole was quickly produced in the amalgam and the milling was allowed to continue until the flake was thinned by the ion beam. Figure 5b shows a micrograph of the thinned region.

Due to the large difference in appearance between the oxide powders and the amalgam, the material of interest could be easily identified and the polishing/milling procedure adjusted to give the best results. It is believed that this will be equally true of other ceramic or low conductivity materials such as semiconducting metalloids or geological materials. The large difference in the milling rates usually resulted in the ceramic material being much thicker than the amalgam. This was partially overcome by masking the amalgam by coating the surface of the sample periodically with photo-resist and using lower milling voltages. However, despite these modifications the ceramic powders still proved to be difficult to thin unless care was taken during the milling step.

Metallic Samples

To determine the applicability of the technique to metallic materials, Cu-Cr powder was dispersed in the amalgam and samples were made for TEM and SEM observation. The powders were somewhat harder to identify in SEM mounts than the ceramic superconductors since Cu is more similar to the amalgam in properties than are the ceramics. Another complicating factor is that the microstructure of the amalgam appears as a fine dispersion of Ag powders, figure 6. However, the powders could be identified quite readily in the SEM using backscattered imaging and in the TEM using energy dispersive spectroscopy. Although no quantitative study was conducted, a surprisingly large volume percentage of Cu powder could be mounted in a single amalgam capsule, with the probability of producing thin area in the Cu powders increasing as the ratio of powder to amalgam increased. The polishing
Figure 5. A flake of Bi$_2$Sr$_2$CaCu$_2$O$_x$ superconductor. a) Low magnification showing the flake mounted in the amalgam after milling. b) TEM micrograph of a grain boundary in the flake. Arrow shows an impurity phase at the grain boundary. An amorphous layer at the edge, due to the ion milling, is also visible.

Figure 6. Micrographs taken using backscattered electron imaging comparing the microstructure of a) the amalgam and b) Cu-Cr powders mounted in the amalgam. Note that the microstructure of the amalgam appears as a fine dispersion of Ag alloy powders, making identification of the sample powder difficult using secondary electron imaging.

Characteristics of the bulk samples for SEM observation were quite satisfactory although some smearing of the amalgam over the powders was observed. This could be removed easily by lightly etching the surface. As for the ceramics, the results of TEM sample preparation experiments once again showed preferential sputtering; for larger particulate matter this effect was partially offset by low angle sputtering and mechanically dimpling to extremely thin sections or to perforation before ion milling. Small powders seemed to be more conducive to producing thin area than large powders. Figure 7 shows typical SEM and TEM samples.
One concern associated with the mounting of metallic powders was the possibility that the Hg in the capsule would alloy with the sample powder rather than the Ag alloy powder. To investigate this, the interface region between the Cu-Cr powders and the amalgam was examined closely. This interface region is shown in figure 8a. No attack of the powder is evident, and energy dispersive spectroscopy (EDS) analysis failed to reveal any mixing of the Cu with the Hg, figure 8b. In general, few elements exhibit extended solubility in Hg \[2\]. Therefore, little or no edge attack is expected.

In summary, samples prepared in this manner presented adequate though not ideal specimens for both TEM and SEM examination and had the advantage of good thermal and electrical stability due to the properties of the amalgam matrix.

CONCLUSIONS

In this study, dental amalgam was used as a mounting medium to hold small particulate samples of ceramic and metallic materials. It has been shown that:

1. Dental Amalgam offers a number of advantages over other techniques presently being used to prepare samples for examination using TEM and SEM. It is quick, easy, allows good edge retention during polishing with little smearing, is conductive, and allows small particulate to be examined without crushing.

2. The major problem when using dental amalgam is related to the different sputtering rates of the the amalgam and the sample. Care therefore must be taken when ion milling to prevent loss of the sample before electron transparency is reached.

3. Ceramic materials are easiest to identify when mounted in amalgam. Metal
Figure 8. Interface region between amalgam and Cu-Cr sample powder. a) SEM micrograph. No alloying with / attack of / the sample powder is evident. b) EDS analysis across the interface region showing that no mixing of the Hg with the Cu-Cr powder occurs during trituration.

powders present some difficulties in positive identification due to the considerable amount of morphological detail generated in the relatively inhomogeneous amalgam. However; reasonably good mounts can be prepared with some attention to detail and the resulting specimen mounts should possess good thermal and electrical stability.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. J. Consamus DDS for his assistance in providing the initial amalgam capsules and for the loan of the amalgamator used in this study. One of us (L.S.C.) would like to thank J.W. Zindel for his helpful suggestions. The authors gratefully acknowledge I.E. Anderson, D.K. Finnemore, R.W. McCallum, J.E. Shield and S. Arrasmith for providing samples, and K.L. Breitbach for assistance in the preparation of this manuscript. This work was performed at the Ames Laboratory, Iowa State University and was supported by the Director of Energy Research, Office of Basic Sciences, U.S. DEPARTMENT OF ENERGY under Contract No. W-7405-Eng-82.

REFERENCES

1. Mixing instructions from Kerr USA, manufacturer of the amalgam used in this study.