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Issues of Compatibility Between Nanomaterials and Aluminum Scanning Electron Microscope Mounts

by Donovan Harris

ARL-MR-601 **December 2004**

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14. ABSTRACT

Aluminum mounts are ubiquitously present in scanning electron microscope (SEM) laboratories. They are an inexpensive light material with good conductivity properties, and are generally compatible with conductive adhesive products. In the course of using aluminum mounts to examine nanoscale materials, some compatibility issues were revealed. One limiting issue was charge conduction. Nanoscale materials can be a more efficient conductor of electrons than the aluminum mount with its layer of oxides. The design of the SEM can constrain charge dissipation. These topics are discussed in summarized form using examples from nanotube dispersion research.

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1. Summary

During the course of working with nanomaterials, it was found that aluminum mounts used for electron microscopy present several technical barriers to good and efficient data generation. This included mounts with polished surfaces. These "as received" surfaces of the aluminum mounts were generally not suitable for use with nanomaterials. The discussion centers on work done on dispersing carbon nanotubes, as it most fully documents the issues found. Three of the solutions include: examine all mounts at 10,000–100,000 magnifications before use; plasma coat the surfaces with either a gold or platinum alloy; and/or add a "grounding" strap on the surface of the mount or mounted material.

2. Introduction

The scanning electron microscope (SEM) was used as a quick test method for determining the efficacy of different procedures to disperse carbon nanotubes. The aluminum mounts used presented a variety of issues, which for the tube dispersion work were mostly time consuming in their effect. These issues have produced a more destructive effect with other nanomaterials. As the tube dispersion data is the most comprehensive, only those results are discussed. The report addresses some issues arising from mechanical and chemical finishing of the aluminum mounts. The lathe finished mounts were known to be less than ideal for tube measurements, but thought to be sufficient for assessing processing efficacy, and any precise measurements would be done using either smaller satin finished mounts, or copper grids. All of those are shown to have limiting flaws. A brief discussion of SEM design contributions to surface charging is presented as several aspects of the mount problems are instrument design related. The remediation of these issues presented is based upon in-house capabilities and the requirement to be able to support multiple parallel projects. One recommendation is design specific, while the remainder are applicable to all SEMs.

3. Procedures

Carbon nanotubes were dispersed using a variety of instruments (to be detailed in a separate report). The dispersion media were pure solvents, solvents plus surfactants, and resins. A portion of the solvent dispersions were withdrawn using a Pasteur pipette and then placed upon a solvent sonically cleaned aluminum mount. The individual mounts were held within a 2-in diameter Petri dish and covered using ribbed watch glasses. The more volatile solvents were allowed to evaporate off under ambient conditions. The low volatility samples were evaporated overnight at room temperature under low vacuum. The resin dispersions were hardened, mechanically fractured, mounted using colloidal graphite media, and then vacuum dried over night. All samples were examined using a Hitachi S-4700, field emission SEM (FE-SEM). The emission current (source current) was 2 µA for all micrographs presented, except for those associated with the elemental analysis by energy dispersive spectroscopy (EDS). The latter were done at 12 µA. All post processing of the micrographs was performed using Adobe's Photoshop 7.01.

4. Results and Discussion

Most aluminum mounts for use in SEMs are machine lathed. That process produces the rough surface topography seen in figure 1. Evident are large areas into which nano-sized materials could be deposited and hence obscured. The surface charging of loose surface debris is typical, even after solvent cleaning in a sonic bath. The charging at the upper right of figure 1 was produced by an aluminum snag or spall. While not a surface for making measurements of

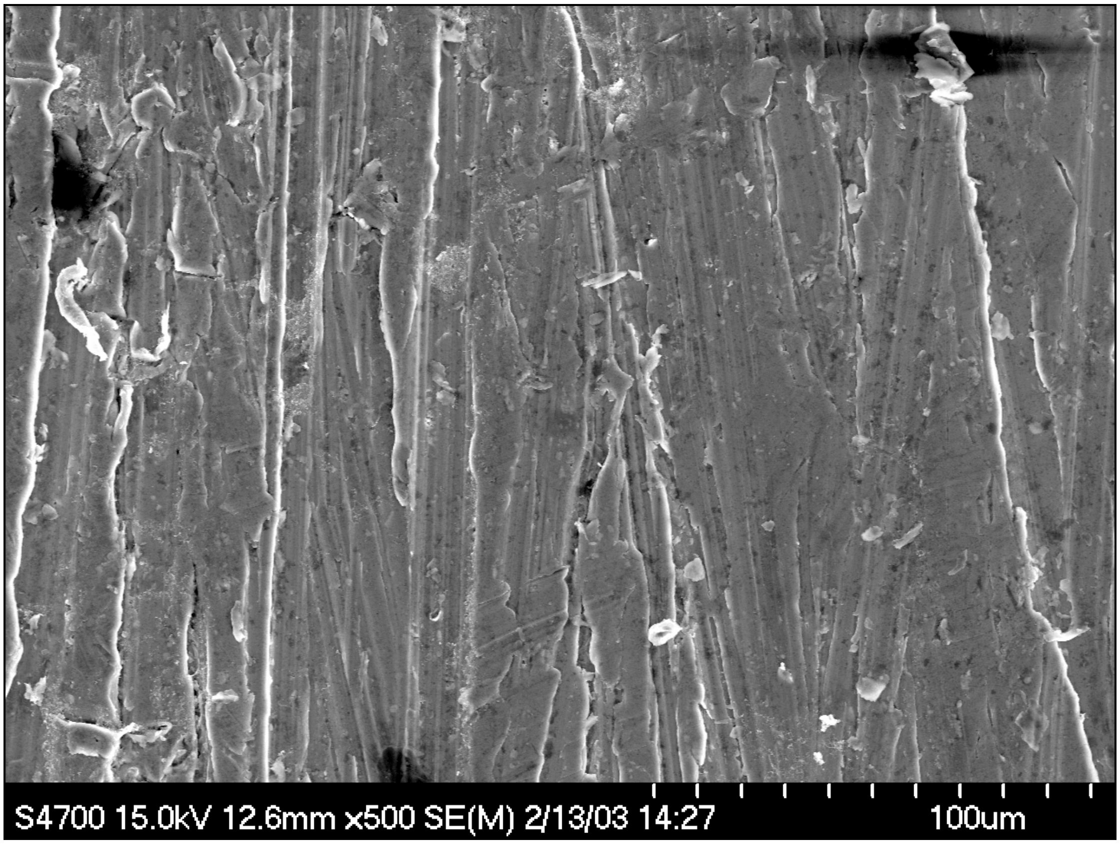

Figure 1. Typical lathe finished surface.

nanoscale materials, it was thought to be satisfactory for assessing tube dispersions (figure 2). Here, a small mat of partially dispersed tubes readily over lies most of the disparities of the aluminum mount surface topology. The image in figure 2 was manually modified using its histogram to adjust the black and gamma values. The differences in the white levels are mainly a function electron transport along the tubes to ground.

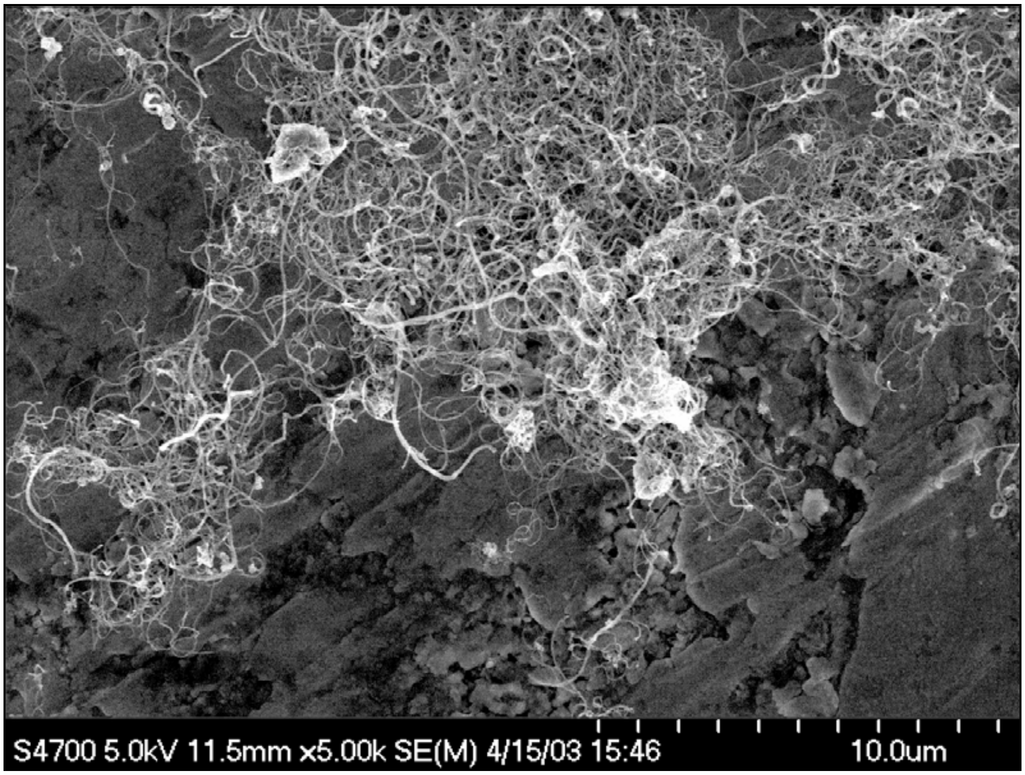

Figure 2. A mat of nanotubes on a lathe finished surface.

A partially dispersed gnarl with a mat of nanotubes can be seen in figure 3; another gnarl is found in the upper left. The tube mat has effectively diminished the edge effects evident in figure 1. However, the number and size of white/hot spots increased out of proportion with the change in magnification. Were these spots small tube gnarls, oxidized aluminum charging, or residual manufacturing impurities? The tubes had been purchased as meeting a specific level of purity, for targeted application purposes. Typically, the impurities are entrapped by the tube gnarl, but tubes in the gnarl can be entrained in the impurity. What should have been a quick look evolved into a more detailed analysis. The majority of the white spots were a result of charging on the aluminum spalls, which can act as crude capacitors. The nanotube mat has better transport properties, so a charge builds at a surface defect. The upper left gnarl experienced some charging, along with geometry-based electron scattering, to cause the observed white level. Similar effects are seen to a lesser extent on the large partially dispersed gnarl at lower center. These determinations required an additional four hours on the FE-SEM. The offline processing and analysis time changed from the projected 90 min to a full day.

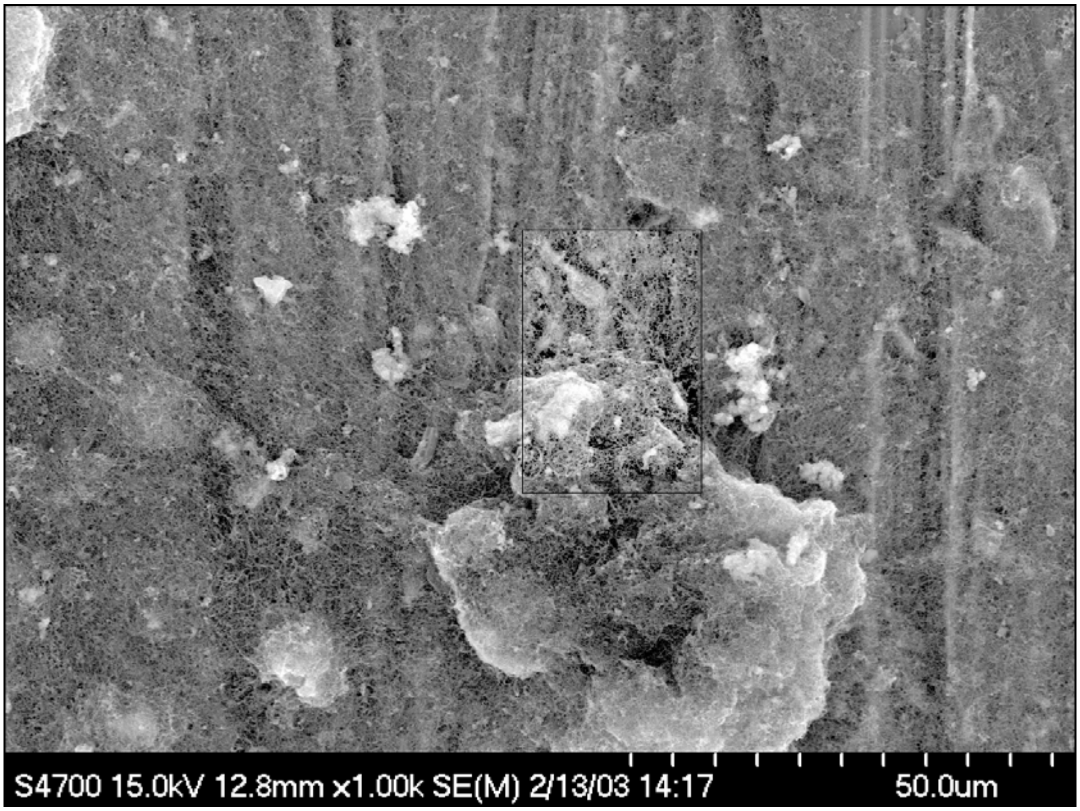

Figure 3. Nanotube gnarls and mat on lathed surface.

Once it was known that the issue was not the tubes themselves, it was decided to change mounts. The use of film coated and noncoated grids proved to be unproductive for this stage of the dispersion processing. The two main problems were film-solvent compatibility and grid usability following tube deposition. Film-solvent compatibility will be considered self-defining for this report. The issue of usability in this context is broader than simply being able to use the grid mounted sample in the FE-SEM, which was not possible most of the time. Mostly, the dispersed tubes ended up everywhere except on the top surface, which would be populated by tube gnarls of various dimensions. The grid samples simply were not representative of the dispersions. As an alternative mount was available, further efforts with the grids were not pursued.

The alternative mount was an aluminum cylinder with a smooth but not polished surface, referred to as a slug by some suppliers. A micrograph with a magnification of 50× shows a range of tube gnarls (figure 4). The surface has neither large disparity nor obscuring edge effects. The inefficacy of the dispersion process is readily evident. Only the gamma value of the micrograph has been adjusted.

Increasing the magnification to 1,000× (1k×) produced the surface charging seen in figure 5, as evidenced by large dark streak areas originating at the lower right of the tube gnarl. Several smaller dark areas, seen on the surrounding surface, exhibit no such behavior. If the solvent

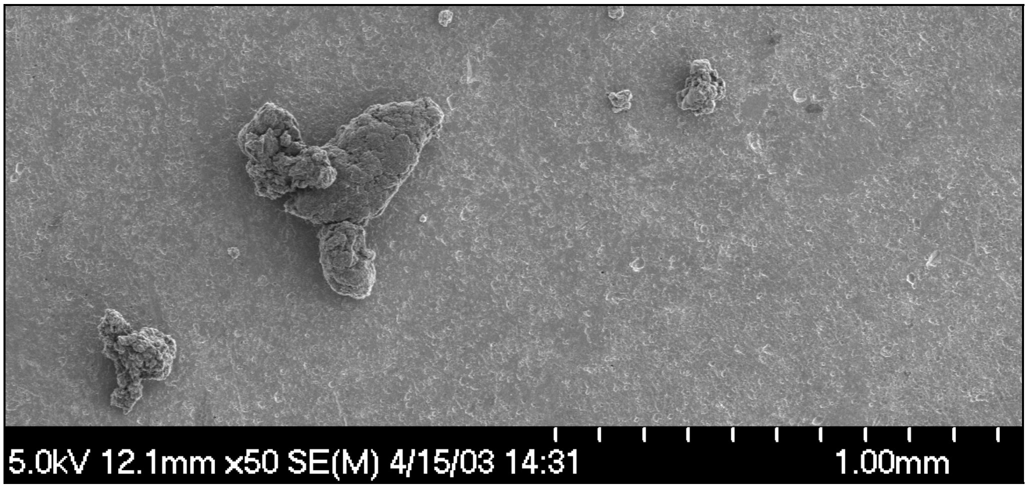

Figure 4. Cylinder/slug mount with tube gnarls.

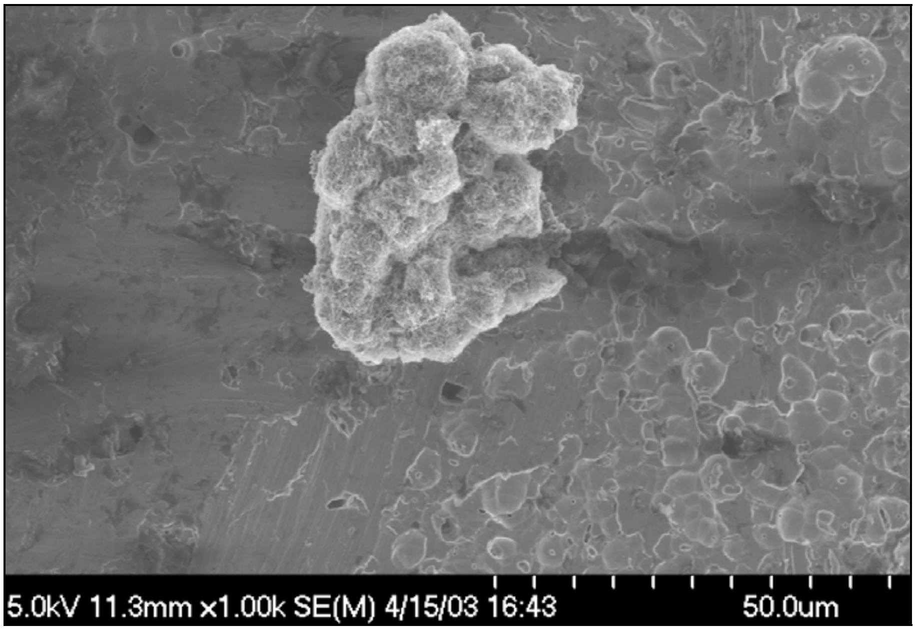

Figure 5. Charging at gnarl with higher magnification.

sonication cleaning process was not effective, that would explain the wet looking dark spots. Contrast that with a lathed finished mount at 1k× and 2k× (figure 6) where no charging is seen.

If the rate of electrons impacting on the surface is approximately equal to the rate of electron drain at the ground point, then figure 5 type surface charging will not occur. The observed surface charging is not solely the result of surface conductivity. At constant emission current, the other factors are the beam voltage and the ground path. As stated earlier, except for EDS, all

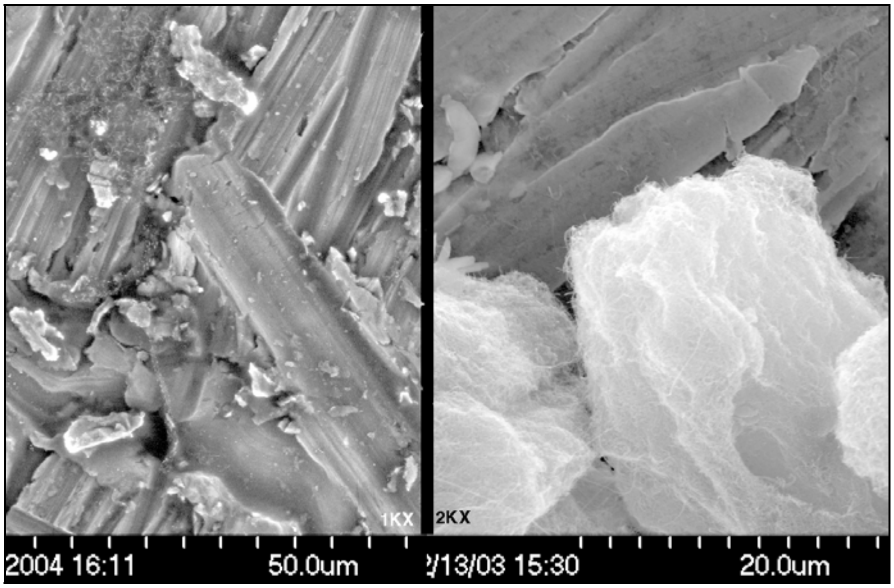

Figure 6. Two lathed surfaces with nanotubes at 20 kV and higher magnifications.

the specimens were examined at the same beam current, 2 µA. While figures 4 and 5 were at 5 kV, figure 6 is at 20 kV.

Earlier SEMs generally had a grounding point that contacted either the surface of the mount or the side of the mount. This was a necessity caused by the higher beam currents required. The sources were dimmer and the detectors inefficient and fragile. Sample charging could take out part of the detector circuit. With source and detector improvements, the mount grounding strap vanished, and the stage base became the sample grounding point. For those specimens with severe charging sensitivity, biological and polymeric, variable/low pressure SEMs were built. The S-4700 is a high vacuum system.

For the two aluminum mounts, the ground paths were physically different, as shown in figures 7 and 8. Except for the small brass piece, figure 7 shows the physical configuration for the lathe finished aluminum mount assembly. The 15-mm mount is screwed on to the T-mount. A loading bar screws into the base and the bottom flanges lock the assembly into the stage, after which the loading bar is unscrewed and withdrawn from the sample chamber. The cylinder type mounts (figure 8) were placed in a multiple holder, which in turn was mounted to a T-base adapter. The threaded post has a 6-mm diameter, while the solid post is 3 mm. The lathed mount is 6.5 mm thick with a 15-mm diameter. The multimount is 10 mm thick with a 31-mm diameter. That balance did not occur with the slug type mounts until the acceleration voltage was 20 kV and the emission current was set to 12 µA. While local charging is evident in figure 9, there is no surface charging seen at 5 kV and 2 µA. Here, the surface is the superior conductor, while in figure 5 the tube gnarl has that property.

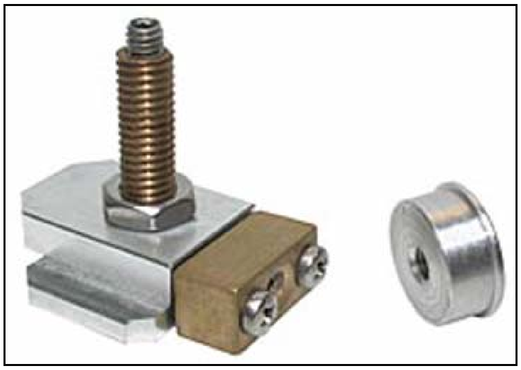

Figure 7. Hitachi T-base (left) with 15-mm mount (right). Brass block is not standard.

Figure 8. Multimount with slug mounts and T-base adapters.

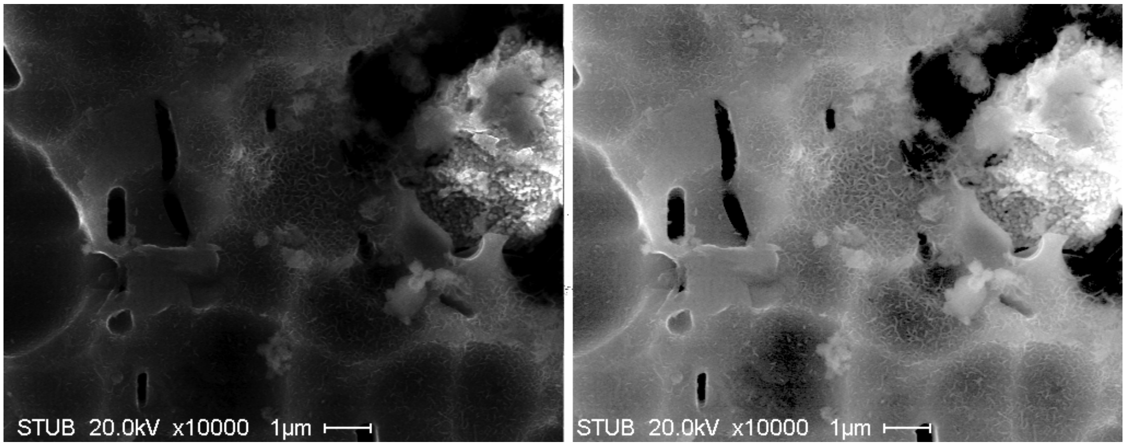

Figure 9. Mount at 10k× magnification, a beam voltage of 20 kV, and emission current of 12 µA.

Using higher beam values only worked in a limited number of instances. When the nanotubes were dispersed in resin, a superior conductor was encased in an insulator, which was mounted on a good conductor. A uniform dispersion of tubes will mitigate those charging effects, especially if coupled with increased surface conductivity of the mount. In figure 10, a composite of two micrographs illustrate localized charging of carbon nanotube filled resins. The center portion of the left-hand panel was gamma corrected for better visual clarity. The lower area is mostly the surface of the filled material and the upper area is a fracture plane. The existence of a plane coupled with the nanotubes minimizes charging in that region. With an increase of beam voltage and magnification, charging of the resin and "arcing" between tubes occurred, as shown in the right panel. The resin charging is obvious. The "arcing" is limited to the center left of the panel, and to the right light grey triangular patch and involves five nanotubes. Those nanotube paths were not capable of transporting the excess electrons.

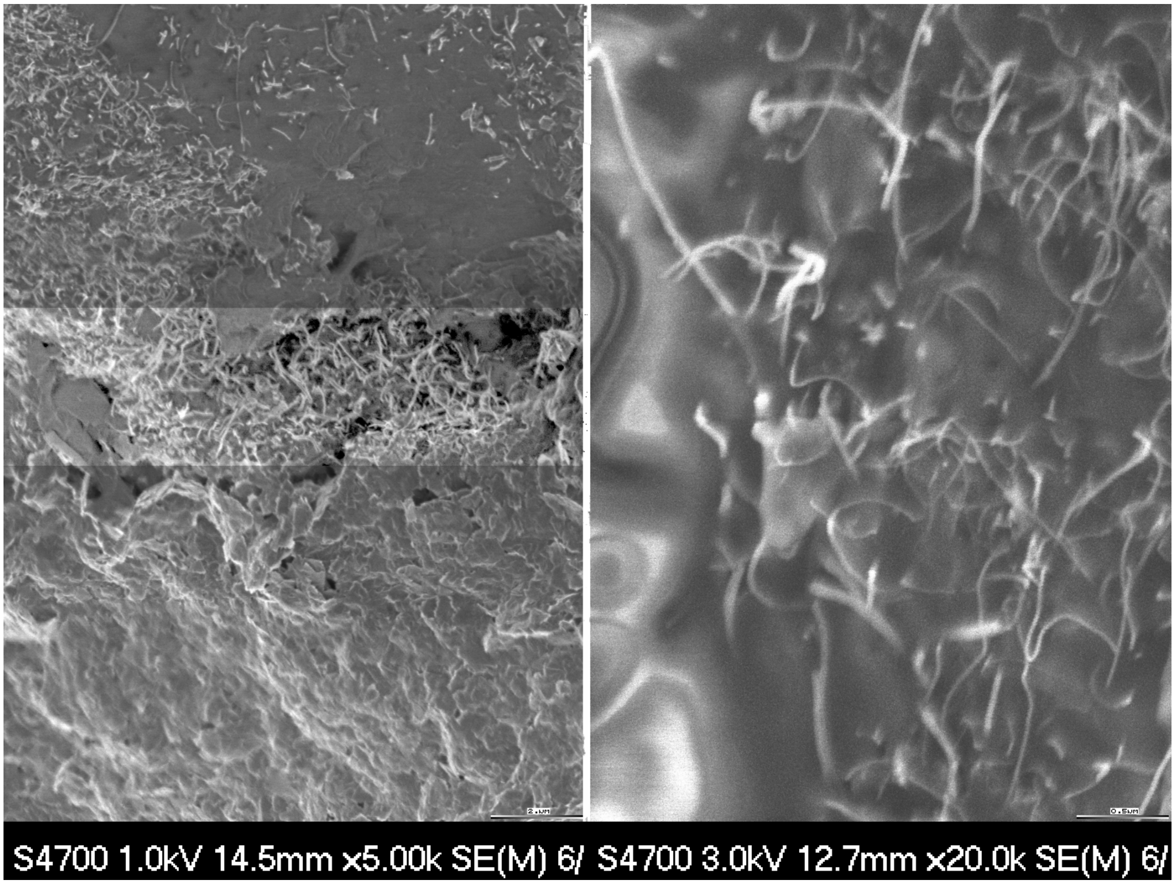

Figure 10. Nanotube filled resin at two magnifications and acceleration voltages. Emission current was 2 µA.

There were two reasons for using a flat mount and not a vise or clamping type mount with the filled resins specimens. First, the topography of the films was too rough for good contact except at isolated points. The second reason was electrical. Using a vise or clamping mount would physically produce a conductor-insulator-conductor-insulator-conductor setup. The charge conduction paths for the specimen in figure 10 were mainly through the resin matrix via the nanotubes to the surface of the mount. By using a vise or clip, all of the conduction paths would be internal to the filled resin film.

Polished SEM mounts, while providing a uniformly smooth surface, come with a different set a problems. Figure 11 is a compound micrograph of an aluminum mount and a nanotube filled resin. The identity of each only becomes evident in time.

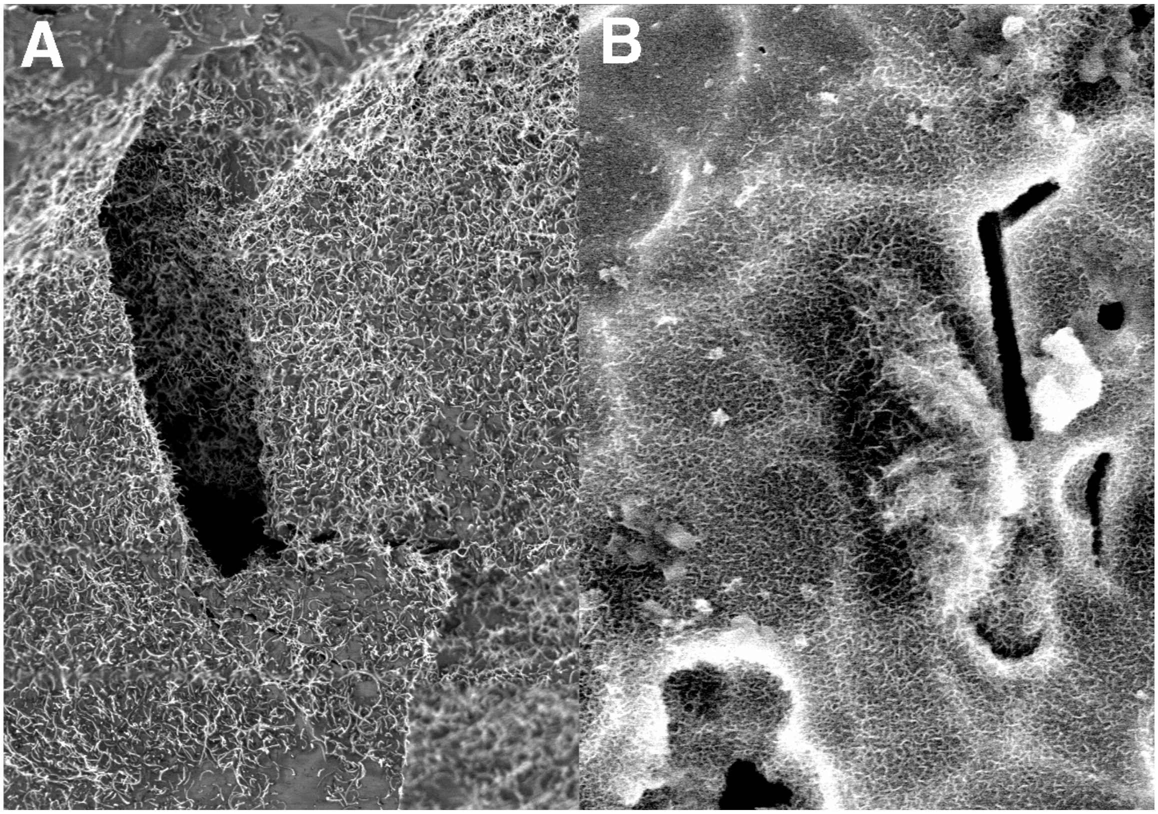

Figure 11. An aluminum mount and a sample of tube filled resin. Which is the mount?

Is the surface labeled B in figure 11 sufficiently conductive to avoid charging and collect a good micrograph of nanotube dispersions? How much material will be lost into the voids in the surface of side B? Barring a thorough inspection before use in a SEM, these are hidden faults. The B surface was being used as the control surface for the examination of three dispersions. The stage rotation control arrows correctly indicate the direction of the image rotation, but the stage rotates opposite. With a single mount, that isn't an issue. Using a multimount, it is often a forgotten issue until the wrong sample appears on the screen. In the course of trying to find nonexistent nanotubes, the features shown were found. The scale of those features is consistent with results reported for nanotubes pretreated in the same manner as what should have been the first dispersion sample. The rotation issue clarified itself when the fourth stub was rotated into position and tube gnarls were seen. To achieve a better understanding of the surface in B, it was decided to perform an EDS elemental analysis of three separate areas.

A real problem was revealed when the EDS analysis was performed on the mount. The outer mount areas possessed a uniform alloy composition, while areas of differing chemical composition were found across the center area of the mount. Figure 12 shows the EDS spectrum of one such area with an overlay of its original and enhanced micrograph. Overlaid onto that spectrum is a second spectrum, black, at the same magnification, but from an area beyond the center area.

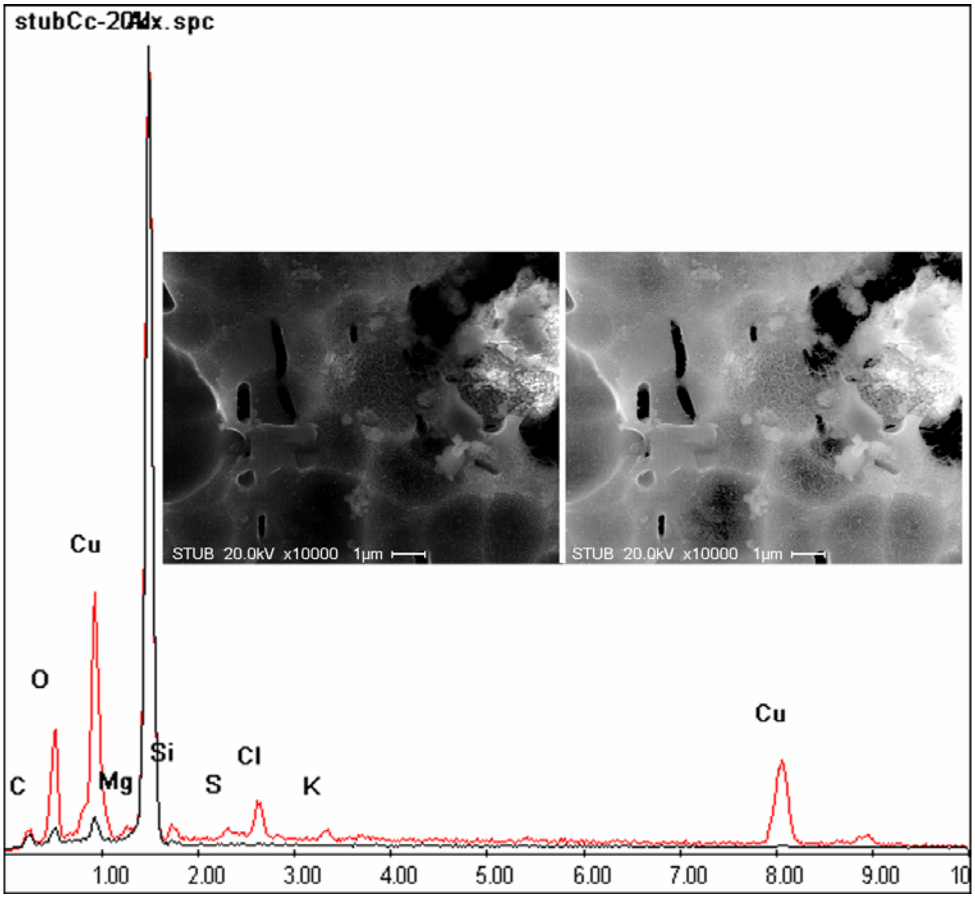

Figure 12. EDS spectrum and micrograph of a polished slug mount.

The red spectrum has two copper (Cu) peaks; the left hand peak is a Cu L line also seen in the blue/purple spectrum, while two right hand peaks in red are the Cu K doublet lines. This shows that, for the bulk alloy, there was not a sufficient Cu concentration to produce a K line, nominally about than 0.1 weight-percent. Although methylene chloride, CH_2Cl_2, was used to sonically clean the mounts, no detectable levels of chlorine where found on the regular surface. The existence of unanticipated chemical species threatened the capability to accurately characterize functionalized materials. The cause of the physical and chemical differences was immaterial to the project and not investigated further.

5. Conclusions

Most of the discussion has concerned issues essentially peripheral to evaluating the efficacy of different techniques to disperse nanotubes. Addressing what were side issues at the time did impact the dispersion test schedule, but proved to be a cost effective effort for the overall program. At this stage, the sample sizes were in the microgram to milligram range. The next stage was to scale up to using tens of grams dispersions. At this time, carbon nanotube prices average about $100 per gram for half a kilogram. This is substantially less than the cost at the initiation of the program. Examining all the mounts prior to use is a simple but impractical solution. Two equally simple solutions exist. The first is to change the T-base used so that direct surface grounds can be added as needed without impeding the normal functionality of the scope. Nor is there any modification to scope. The base shown in figure 13 is a currently available alternative to the base originally provided.

Figure 13. T-base with brass adapter, which permits the use of sample direct grounds.

Secondly, existing polished mounts will be plasma coated in-house with either gold or platinum as piggy back efforts. Those coatings will improve in the examination of functionalize materials, filled resins, and polymer thin films. In some instances, the use of a variable pressure FE-SEM will be required, but not as a standard requirement. An alternative to plasma coating might be the use of gold leaf to overlay the surface of the mounts, using a thinned conductive adhesive interface layer. While gold leaf is cost effective, the time required to achieve the skill level required to handle and apply the leaf is difficult to justify.

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