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# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Chemical Sciences Division

### Electrocladding of Ceramic Superconductors

T.W. Kueper  
(M.S. Thesis)

December 1989

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# Electrocladding of Ceramic Superconductors

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(M.S. Thesis)

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## 1. Introduction

### 1.1 Applications

High critical-temperature superconductors have recently been demonstrated to present many technical challenges regarding their actual application in devices. Aside from the problem of bulk samples exhibiting critical current densities that are much lower than expected, the corrosion of the superconductor that is seen on surfaces exposed to air and the difficulty involved with making electrical contacts are problems that will have to be dealt with. The large surface areas of wires or filaments make the control of surface conditions particularly important in these applications. Other concerns for superconductor materials include their lack of toughness and ductility, and the possible presence of defect regions which would require alternate conduction paths or temperature stabilization. The electrodeposition of metals holds promise as a way to coat bulk superconducting objects, providing a solution for many of these problems.

Possibly the foremost concern for superconducting products (particularly  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ) is their sensitivity to water and water vapor. For any oxygen content ( $0 < \delta < 1$ ), the superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is destroyed upon exposure to water or water vapor. The onset of superconductivity in exposed samples is seen to occur over a much broader temperature range than in the unexposed state, with appreciable resistivity remaining near absolute zero<sup>1</sup>. Experiments with epoxy coating show that it provides only limited protection; after extended exposure to humidity, an epoxy coated sample will exhibit loss

of superconductivity<sup>2</sup>. Apparently then, a coating must protect against any atmospheric penetration to be effective; even a metal coating must be completely free of connected porosity. The noted progression of corrosion into test samples indicates that atmospheric moisture diffuses through the superconductor, endangering the entire volume of the sample. The corrosion products are  $\text{CuO}$ ,  $\text{O}_2$ , and  $\text{Ba(OH)}_2$  which converts to  $\text{BaCO}_3$  upon reaction with atmospheric  $\text{CO}_2$ . During corrosion, needle shaped crystals of barium carbonate form, accompanied by slow crack growth and the eventual disintegration of the sample<sup>3</sup>. Obviously, superconducting products will require protection from the atmosphere if they are to be reliable for any length of time.

The possibility of mechanical forces acting on the superconductor is another concern. Conventional extrusion techniques for fabricating useful wire are inadequate for the brittle ceramic oxides. Mechanical reinforcement against external stresses would have to be provided by a coating of some sort. (Although the formation of a composite wire by surrounding a normal metal core with superconducting material has been proposed as a way of reinforcing superconducting wire<sup>16</sup>, the metal would be much more useful in taking up bending stresses if it were coated on the outside of the wire, as is the case in this electrodeposition research.)

Providing electrical contact to the bare surface of a superconducting wire would also be a great difficulty in building a device. A product which is coated with a normal metal would be much easier to work with, as conventional technology could be used whenever a contact needed to be made. Several methods for making low resistance contacts to the new high  $T_c$  superconductors have been developed<sup>4-7</sup>, but



most involve high temperature and high vacuum processes, and are not well suited to coating wires (See section 1.2).

Metal coatings on superconducting wires would be very useful for insuring that a wire with defect regions would be able to carry current with some stability. Because superconducting wire may contain non-superconducting regions and cracks, a parallel conduction path through which the current can flow when necessary is desirable. A coating with high thermal conductivity, such as aluminum or silver, would also serve as a heat sink: Heat which may be generated electronically in non-superconducting regions could be withdrawn from the sample before the critical temperature is exceeded in the area of the defect and superconductivity is destroyed.

Most coating methods available to solve these problems involve heating the superconductor during the coating process. This heating may affect the oxygen content as well as degrade the superconductivity near the interface; a room temperature process would have many advantages over processes which require elevated temperatures (See section 1.2). For the same reasons, methods which require heat treatments after the coating is applied are also not desirable.

The goal of this research was to develop room temperature methods for coating metals onto bulk superconductor objects to provide protection and electrical contact. Aluminum and silver have been electrodeposited onto samples of the superconductor and it appears that these coatings should be useful for solving the problems in applications that are outlined above. The quality and continuity of the coatings have been examined, as has the interfacial resistance.

## 1.2 Advantages of Electroplating

Electrodeposition has many possible advantages as a coating method. Perhaps most importantly, the process could be a low temperature alternative to other coating methods (All plating research to be presented here was carried out at room temperature). Competing methods for coating the superconductor often involve either elevated temperatures during coating or heat treatments after the coating is applied. The superconductor has a lower oxygen content at higher temperatures; oxygen must diffuse back into the superconductor during cooling. If a coating is applied at a high temperature, it can act as a barrier to this oxygen diffusion. In addition to limiting the oxygen supply in this way, heating during a coating process increases the danger of a chemical reaction with the superconductor, and also of interdiffusion between the coating and the ceramic, which may degrade superconductivity.

A sample process is the wire-drawing of a normal metal tube filled with superconductor powder<sup>8</sup>. This particular method for fabricating a composite superconducting wire requires annealing afterwards at 900°C. The necessity of protecting the superconductor during the anneal prompts the consideration of such measures as the addition of a diffusion barrier, high pressure oxygen processing, the addition of an oxygen donor to the core, or even the use of a deliberately porous cladding material<sup>8</sup>. If plating is done at room temperature, after any heat treatments, then the need for a diffusion barrier at the metal-superconductor junction is eliminated, as is the problem of a limited oxygen supply to the superconductor during cooling. The superconductor

may be annealed to the ideal state and then clad as a final process.

The electroplating of both aluminum and silver will be considered here. There exist many room temperature plating baths for aluminum (see section 1.4). Because of the electronegativity of aluminum, plating solutions must be completely non-aqueous; the baths that have been developed are therefore ideal for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and no work needs to be done to find benign baths. Although the need for a controlled atmosphere may seem to be a problem for composite wire fabrication, aluminum electrodeposition is actually well suited geometrically for wire cladding (compared to high vacuum processes for example). A patent has been granted for an installation designed for continuous electrodeposition of aluminum from an Al-organic electrolyte onto elongated objects. The electrolyte is circulated through the cell in the direction opposite to the movement of the objects, and is sealed from the outside atmosphere<sup>9</sup>. The ease and availability of such continuous coating methods need to be considered when comparing the merits of different processes.

Aluminum is a good choice as a cladding material for many reasons. It is economical, has good mechanical properties, and is corrosion resistant. Aluminum may be the ideal material for use as a parallel conductor, because while it has a room temperature conductivity of 62-64% of the International Annealed Copper Standard (IACS), the resistivity of aluminum falls below even that of copper at temperatures below 60°K, making it extremely competitive for cryogenic applications<sup>10</sup>. The thermal expansion coefficients of aluminum and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are also well matched<sup>11,12</sup> (Fig. 1). The curves are closest together in the temperature range between room temperature and 77K, the

critical range for thermal cycling. Some of the strain that would be accumulated during cooling between room temperature and 140 K would be compensated for upon further cooling, as curves cross at this temperature.

Silver may have one advantage over aluminum as a superconductor cladding material because of its minimal contact resistivity and reactivity. Research on Fe layers that were deposited on cleaved crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in ultrahigh vacuum has shown that reactive metals (such as Fe and Al) may cause problems by forming reaction layers. In the Fe experiments, an insulating layer of Fe-O formed by withdrawing oxygen from the superconductor. Barium was also found to diffuse out to the surface of the Fe layer, depleting the superconductor of barium<sup>13</sup>. Aluminum may cause similar reactions; it may be necessary to use a nonreactive metal such as silver to avoid the formation of a reaction layer. Silver is also known to have good oxygen permeability, which would be an advantage if silver were used as a coating in an application which requires reoxidation of the superconductor after the coating is applied. This property would not be as significant for room temperature electrodeposition, however, because reoxidation after the coating is applied may not be necessary.

A thin primary silver coating with a thicker aluminum layer plated on top of the silver may represent an optimally useful coating; in this arrangement the low interfacial resistivity and low reactivity of the silver can be taken advantage of without sacrificing the economy, efficiency, and mechanical properties of an aluminum coating.

### 1.3 The Bulk Superconductor

Conventional powder processing for forming bulk  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  uses  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  as starting materials and includes a calcination step and a sintering step (see experimental procedure).  $\text{BaO}$  or  $\text{BaO}_2$  reacts more rapidly than  $\text{BaCO}_3$  and has the potential to reduce calcination times, but these compounds are hygroscopic and therefore not suitable for superconductor formation<sup>14</sup>. Sintered products which are from 90-95% of theoretical density can be obtained from conventional powder processing.

A variety of processing methods for bulk superconductors have been developed which provide some hope of fabricating working products from the fragile ceramics. Several methods specifically designed for fabricating wires or filaments from superconducting material exist.

Organic binders have been combined with powder to produce flexible superconducting tape and products with other shapes<sup>15</sup>. A powder and binder coating have also been applied to a normal metal core to produce a flexible wire that can be melt processed and heat treated to form superconducting composite wire<sup>16</sup>. This product would still require an outside coating for atmospheric protection and possibly for greater reinforcement against bending stresses.

Melt processing has been used to create dense wire-like products from green bodies of the superconductor: Short sections of approximately 1 mm diameter wire can be produced by "melt drawing", in which a pressed superconductor bar is held in air over a gas blow torch until the center melts, at which time the ends are drawn rapidly apart, reducing the section up to 88%<sup>16</sup>. A variation is "melt spinning", in

which a molten droplet from a torch-heated bar is spun off a heated, rotating mandrel to produce a ribbon. The products from both of these techniques have in general a less porous microstructure than that obtained from conventional processing. After subsequent heat treatments the products also exhibit electrical and mechanical properties superior to those of free-sintered samples.

While these methods have been studied primarily using the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , many should be applicable to higher- $T_c$  superconductors as well--in any case, superconducting wire products should be improved by electrodeposited metal coatings.

#### 1.4 The Aluminum Plating Bath

Aluminum cannot be plated from aqueous solutions because water will be reduced before aluminum. For this reason, numerous studies have been conducted on methods of non-aqueous plating. Plating from molten salt solutions such as  $\text{AlCl}_3\text{-NaCl}$  is common; however, most molten salt baths require elevated temperatures. In such melts the growth of the deposit tends to be highly dendritic, so that current densities must be kept very low in order to obtain a smooth coating. One study of  $\text{AlCl}_3\text{-NaCl}$  melts found a current density threshold for dendritic deposit formation was  $1\text{mA/cm}^2$  for pure solutions<sup>17</sup>. (This value could be improved to 20-25  $\text{mA/cm}^2$  with the addition of  $\text{HCl}$ , which was thought to provide  $\text{H}^+$  reduction as an alternate reaction at the tips of the dendrites.)

A more promising method of aluminum electrodeposition involves the use of organic solvents. Solvents such as ether or aromatic hydrocarbons, which contain weak coordination centers, have strong

enough interaction to dissolve the solute, but these interactions are weak enough to allow Al to be reduced from unsymmetrical aluminum-containing complex ions<sup>18</sup>. Baths based on such solvents include an  $\text{AlCl}_3/\text{AlBr}_3$  mixture in ethyl bromide and benzene<sup>19</sup>, and  $\text{AlCl}_3$  with  $\text{LiAlH}_4$  in ether (known as the "NBS bath"<sup>20</sup>). The volatility and flammability of ether make research on alternate solvents attractive. The replacement of part of the ether with a quaternary ammonium salt has produced good deposits with a significant increase in safety<sup>21</sup>. The complete replacement of ether with a tetrahydrofuran (THF) and toluene mixture has also been studied<sup>22,23</sup>.

The most successful room temperature aluminum plating bath has been the NBS bath, which consists of approximately 3 M aluminum chloride and .4 M lithium aluminum hydride in diethyl ether solvent. Good deposits have been obtained at current densities of up to 50 mA/cm<sup>2</sup>. The aluminum deposition research presented here was done primarily using the NBS bath.

Stirring has been reported to be both beneficial and detrimental to deposit quality. Early studies found that stirring tended to cause roughness in the electrodeposit<sup>21</sup>. However, larger scale use of the NBS bath showed that agitation was essential to prevent dendritic growth of the deposit<sup>24</sup>. Ultrasonic agitation may also be useful for improving the contact resistance of the plated metal to the superconductor, if intermediate oxide layers become a problem<sup>25</sup>.

### 1.5 The Silver Plating Bath

Because silver, unlike aluminum, is easily plated from aqueous

solutions using well established cyanide-containing electrolytes, there has been little research on non-aqueous silver plating baths. An attempt to use the existing technology and plate the superconductor from an aqueous cyanide electrolyte would require elaborate steps to insure that the superconductor is not corroded. The potential range over which electrochemistry can be carried out in aqueous solutions is also severely limited by superconductor degradation<sup>26</sup>. Clearly, non-aqueous baths must be developed.

A measure of the compatibility of a solvent with the superconductor is the faradaic response of a superconductor electrode after exposure to the solvent in question: Corrosion is accompanied by the formation of an insulating layer on the surface of the superconductor. If the sample is intermittently removed from the test environment so that cyclic voltammetry can be performed on it, a change can be seen in the  $iR$  response as the corrosion proceeds. The insulating layer blocks the faradaic response, leading to a linear  $iR$  response when the surface is completely corroded, and this behavior can be used to define the superconductor electrode lifetime<sup>27</sup>. Lifetimes found in this study ranged from only minutes for acidic solutions to greater than three months for dry air. Satisfactory response was still seen after two weeks in dry aprotic solvents such as acetonitrile, indicating that such solvents would be suitable for silver plating applications.

The solvent that is chosen must be capable of dissolving both a silver-containing compound as a source for silver ions and a supporting electrolyte. The source of silver ions in aqueous technology is usually  $AgCN$ . However, the electrochemistry of non-aqueous systems is very different, and other sources may need to be considered.



The supporting electrolyte, which may be a salt of an alkali or alkali earth metal, serves to increase the conductivity of the solution, reducing the potential difference across the bath. The ions of the supporting electrolyte are not discharged at the cathode, but instead migrate to the region near the cathode surface and remain there, reducing the electric field in the bath. The cathodic polarization will also be increased when the concentration of the supporting electrolyte is sufficiently high<sup>28</sup>.

Cathodic polarization, it should be noted, needs to be large enough to prevent dendritic or even spontaneous deposition. The presence of a potential increase at the surface of the cathode is the only means of controlling the silver ion discharge and preventing spontaneous deposition. The potential of silver in the bath is very high, so that when the ion is uncomplexed there is very little potential increase at the anode, and it is virtually impossible to get satisfactory deposition. In most cases only complexed forms of silver will give a smooth and coherent deposit, as complexing reduces the silver potential in the bath.

The standard aqueous silver plating bath contains  $KAg(CN)_2$  obtained from the addition of  $AgCN$  and  $KCN$  to the solution<sup>29</sup>. Free cyanide is also necessary to increase the cathodic polarization and to raise the bath conductivity. Although these aqueous baths give satisfactory deposits, some research has been conducted on developing less poisonous electrolytes. Complex silver electrolytes formed from iodides, sulfites, pyrophosphates, and ferricyanides have been investigated<sup>29</sup>. The structures of the deposits made from such electrolytes have been examined: Baths containing sulfites and iodides tended to be coarse

grained, while baths similar to the cyanide baths (such as a ferrocyanide-thiocyanate electrolyte) gave finer grained deposits<sup>30</sup>.

Silver complexes can also be formed from simple silver salts and organic acids, but tend to give poorer coatings than cyanide baths. The addition of sodium and potassium tartrate has been found to diminish the roughness of deposits from aqueous  $\text{AgNO}_3$  solutions<sup>31</sup>. The relevant parameter governing growth inhibition has been determined to be the activity of the tartrate monoanion<sup>32</sup>. The complexing method seems to work for organic additives, but is not as effective as the cyanide complexing method.

Hundreds of organic additives have been investigated to determine their influence on the silver electrodeposit structure. In general, the addition of approx. 0.01% of an organic additive improves cohesion and the physical structure of the deposit, and increases the cathodic polarization<sup>33</sup>. However, organic additives tend to be unstable, they tend to be useful only over a narrow concentration range, and their decomposition products can cause embrittlement of the deposit<sup>28</sup>. Organic additives should be avoided if alternate means can be found to arrive at a good deposit.

While many of the mechanisms for the improvement of deposit structure discussed above for aqueous electrolytes may be similar for non-aqueous electrolytes, the chemistry will be very different. Using such solvents as acetonitrile, ethanol, ether, and propylene carbonate, the choices for compounds that will give a suitable silver complex and supporting electrolyte will have to be made using aqueous technology as a starting point. Substitutions will have to be made based on the results obtained.

## 1.6 Optimum Surface Resistivity

A special problem needs to be considered if the normal metal coating on a wire is to be used as a parallel conductor for the superconducting core. A non-superconducting region that must be bypassed (a crack in the superconductor for example) would create corners on the contact surface where the current would concentrate (Fig. 2). Because the current concentration would approach a singularity at such a point, the critical current density of the superconductor would be exceeded in that region.

In order to prevent such instability, the current distribution at the metal/superconductor interface needs to be more uniform. The contact resistance at the interface is a parameter that can control the uniformity of the current distribution. In fact, an optimum distribution of interfacial resistance has been calculated<sup>34</sup> for metal/superconductor contacts of known geometry, based on the critical current density of the superconductor and the bulk resistivity of the metal. In this case the optimum interfacial resistance varies continuously along the length of the contact, reaching a maximum at the corner where the current concentration is expected (Fig. 3).

For the case of a coating used as a parallel conductor for a wire, the geometry (the location of the non-superconducting regions) is obviously not known, and therefore an engineered profile in the interfacial resistance would be useless. The best that can be done in this case is to have a constant interfacial resistance throughout the length of the wire, and to make this resistance large enough to keep the

current density from exceeding the critical value for the superconductor in the region where a crack may develop. The desired interfacial resistance value would depend on the relative current carrying capabilities of the superconductor and the parallel conductor.

## 2. Experimental Procedure

### 2.1 Powder Processing

Samples for aluminum electroplating were made by conventional powder processing (Fig. 4). All starting powders were 99.999% pure:  $Y_2O_3$  (Sigma),  $BaCO_3$  (Noah Chemical), and  $CuO$  (Aldrich) powders were mixed in the proper stoichiometric ratios for the 1-2-3 compound and milled for two hours on a planetary mill in toluene with zirconia balls. The powder was filtered, dried for two hours in a vacuum oven, and then lightly reground by hand. It was then calcined at  $850^\circ C$  for 24 hours. The resultant powder was hand ground once again, and samples of approximately 1.5 grams were pressed at 25,000 psi in a 1/2" die. Thin round pellets with a thickness of approximately 3 mm were formed.

The pellets were sintered at  $940^\circ C$  for six hours in a tube furnace (ATS), with flowing oxygen atmosphere, and then annealed at  $450^\circ C$  for two hours. Between holding temperatures, ramps of  $20^\circ$  per minute were used. The sintered pellets had a final density that was 90-95% of theoretical density, and appeared to be single-phase when viewed in the optical microscope.

Superconductivity was confirmed by observing the Meissner effect on a balloon-encased pellet, which was suspended by a string into a cup of

liquid nitrogen. When a magnet was held up to the cup, the pellet was displaced away from the magnet, demonstrating flux expulsion.

## 2.2 Electrode Assembly

The surface of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  pellet to be plated was sanded using grits of 180, 250, 400 and 600 wet/dry paper with small amounts of kerosene as lubricant. Polishing was done using 6 micron, 1 micron, and in some cases .25 micron diamond paste on a clean sheet of rigid plastic film. The sample was ultrasonically cleaned in toluene between each polishing step. An electrode (Fig. 5) was formed by joining a bent steel rod to the pellet with room-temperature-curing conductive silver epoxy (Tra-con Inc), and then covering all surfaces except the intended plating surface with insulating epoxy (Hardman Inc). The exposed area was circular with a diameter of about one centimeter. Care was taken to insure that the entire front surface of the electrode, including the epoxy border, was planar. In some cases, the electrode was sanded and polished using the sequence described above after the epoxy was applied, in order to create a smooth transition from superconductor to epoxy at the edges of the circle.

Counter electrodes made with 99.999% pure aluminum were fashioned in the same manner, with epoxy covering the side and back surfaces. Exposed areas were the same size and shape as the superconductor electrode to be plated.

Superconductor electrodes identical to those described for aluminum plating were used for the silver plating, and the counter electrodes were 99.9% pure silver. For bath conductivity experiments, similar

copper electrodes were used as the cathode in place of the superconductor.

In all the plating experiments, the superconductor electrode was hand polished again once it was inside the glove box, to remove any contaminated surface layer. It was then cleaned ultrasonically in toluene, still in the glove box, to remove polishing debris.

When pellets were plated on two sides (for interface resistivity measurements), a simpler arrangement was used: The pellet was fitted into a narrow rubber loop with the stripped end of a wire held to the edge of the pellet under the rubber. In this way both surfaces were left exposed; two counter electrodes were used for these plating runs.

### 2.3 Plating Apparatus

All plating, except where noted, was done in a glove box (Vacuum Atmospheres Company) in argon atmosphere. A teflon cap was machined to hold the steel ends of the electrodes with stop screws. The working and counter electrodes were aligned and spaced about 15 mm apart.

In order to estimate the bath conductivity, two platinum reference electrodes were built: Platinum wires were inserted into two glass pipette ends so that the wire tips protruded, and the openings were then sealed with insulating epoxy leaving just the wire ends exposed. These electrodes were spaced 8 mm apart and placed between the working and counter electrodes (Fig. 6). The thin taper of the pipette ends insured that the electrodes would not significantly affect the current flow geometry of the bath.

The plating solutions were held in 50 ml beakers which were raised

and clamped so that the electrodes were submerged. Current was applied using a Potentiostat-Galvanostat (Princeton Applied Research Model 371), using current control. Voltages between all electrodes were recorded using a digital multimeter (Fluke).

#### 2.4 Bath Preparation

All plating solutions, except where noted, were prepared inside the glove box. Crystalline compounds were dissolved using an ultrasonic agitator when stirring was necessary.

Aluminum plating baths were made using a THF-toluene mixture and also using diethyl ether. The THF-toluene bath tended to phase separate and gave inconsistent results, so the ether bath was used for most test samples. The electrolyte consisted of  $\text{AlCl}_3$  (Morton Thiokol, 99.999%) and  $\text{LiAlH}_4$  (Alfa Products).

For silver plating baths, ethyl alcohol, acetonitrile, ether, and propylene carbonate were all employed. The solvents (except propylene carbonate) were opened only to argon atmosphere in the glove box. Propylene carbonate was dried by filtering through heated dry alumina balls and then kept over alumina in the glove box. Electrolytes in the alcohol-based baths included  $\text{AgNO}_3$  (Mallinckrodt, 99.99%),  $\text{NaNO}_3$  (J T Baker, 99.4%), thiourea (Aldrich, 99%), potassium sodium tartrate (J T Baker, 99.7%),  $\text{NaSCN}$  (Sigma), and  $\text{NaBF}_4$ .

Additionally, silver thiocyanate (Aldrich, 99%), silver trifluoromethanesulfonic acid (silver triflate) (Aldrich, 99+%), silver perchlorate (Aldrich, 99%), tetraethyl ammonium perchlorate (Southwestern Analytical Chemicals, electrometric grade) and silver

trifluoro-thiomethoxide (synthesized from the reaction of AgF and CS<sub>2</sub> in sealed quartz vessels) were used in the propylene carbonate baths.

## 2.5 Characterization of Coatings

To test the contact resistance of the electrodeposit for high current applications, larger superconductor samples with the shape of a rectangular parallelepiped were made (approx. 30 mm X 13 mm X 3 mm). Again a steel rod was attached and insulating epoxy was used to create an electrode with a single rectangular plating surface exposed. The electrodeposit was sanded away from the center portion of the sample and two voltage leads were attached in this area with silver epoxy in order to determine if the sample was superconducting. The sample was then clamped on the aluminum-coated ends with large spring-loaded copper conducting rods and the assembly was submerged in liquid nitrogen and allowed to cool. An alternate method of testing the contact resistance of the coating consisted of clamping a double-sided sample between the conducting rods and eliminating the voltage leads; this method had to be adopted when the larger samples had cracking problems. The test current was supplied by a regulated DC power supply (100 amp capability at 9 volts, Kikusui Electronics Corp.).

Both optical and electron microscopy were used to characterize the coatings and interfaces. Polishing sequences as described above were used.



### 3. Results and Discussion

#### 3.1 Aluminum Plating Bath

The aluminum baths tested here were successful at plating an aluminum deposit onto the superconductor. The first bath tested was  $\text{AlCl}_3$  and  $\text{LiAlH}_4$  in THF and toluene. Phase separation appeared to occur during preparation; the  $\text{LiAlH}_4$ , which had been dissolved in pure THF, apparently remained in a separate THF phase that was above and not in contact with the electrodes. While no deposit formed from the lower phase when the current was applied, the addition of more  $\text{LiAlH}_4$  to the already prepared bath resulted in immediate aluminum deposit formation when current was applied.

The one-component ether bath (the NBS bath) did not phase separate and exhibited good plating characteristics. The bath appeared to be stable, plated clean aluminum with no unwanted precipitate formation, and had good conductivity: The cell voltage was .445 V for a current density of  $29 \text{ mA/cm}^2$  (a 20 mA current for a  $.7 \text{ cm}^2$  sample). About half of the voltage drop occurred within the superconductor electrode. Plating current densities could be increased to  $60 \text{ mA/cm}^2$  while maintaining deposit quality. Stirring was found to lead to a rougher deposit surface and therefore was not employed. As the current was switched on immediately when the electrodes were immersed, the black superconductor surface changed to a metallic appearance within seconds, protecting it from any reaction with the bath. Thicknesses of 100 microns were easily obtained.

With the excellent results from the ether bath, no further research

was conducted on alternate baths for aluminum electrodeposition.

### 3.2 Aluminum Deposit Quality

The aluminum coating appears to adhere well. When adhesive tape is applied to the washed coating and peeled slowly away, only a few of the outermost grains adhere to the tape. The coating is smooth and continuous as revealed by SEM. In (Fig. 7), an aluminum layer of uniform thickness is shown adhering to the superconductor.

Magnification of the interface reveals that the throwing power of the bath is sufficient to fill any surface porosity in the superconductor with aluminum (Fig. 8). This penetration creates an interlocking effect between the materials which may be beneficial to the adhesion. Adhesion appears unaffected after thermal cycling to liquid nitrogen temperature, verified with the adhesive tape test. The interface appears to be very clean even at high magnification; no reaction layer between the superconductor and the aluminum is visible at 5700 X (Fig. 9).

The contacts made with the electroplated aluminum were non-ohmic. The contact resistance was approximately  $10 \text{ m}\Omega\text{cm}^2$ , although that value decreased for increased current densities.

### 3.3 Silver Plating Baths

Since dry aprotic solvents were reported to be benign to the superconductor, the solvents acetonitrile, ether, and ethanol were tested for their ability to dissolve silver nitrate. The compound, when

added and stirred ultrasonically at room temperature, most readily went into ethanol, giving an approximately .01 M solution. Acetonitrile and ether had poorer solubilities. Perhaps because of higher silver content, the simple ethanol-AgNO<sub>3</sub> bath deposited silver with more electrode coverage than the other attempts. Although this deposit was very dendritic and surface coverage remained incomplete even with a 20 micron coating, attempts using acetonitrile and ether resulted in almost no electrode coverage whatsoever. Therefore, further attempts at forming an acceptable bath from AgNO<sub>3</sub> and complexing agents were conducted using ethanol as the solvent. (Propylene carbonate was used as the solvent later, but was not tested with AgNO<sub>3</sub> alone.)

Efforts to complex the silver from the simple nitrate bath began with the use of some of the additives that are used in aqueous silver plating technology. For some possible complexing agents, such as NaBF<sub>4</sub> and NaSCN, the addition of very small amounts to the AgNO<sub>3</sub>-ethanol solution caused a fine brown precipitate or colloid to form upon stirring. Attempts to plate silver from these "liquids" were unsuccessful; it is hypothesized that the brown precipitate contained the silver from the solution. Other electrolytes based on ethanol and AgNO<sub>3</sub> were formed using thiourea and sodium-potassium tartrate, organic growth inhibitors that had been successful in aqueous baths. These additives were tried separately and also together in varying ratios. NaNO<sub>3</sub> was also added to some baths to provide a supporting electrolyte (see Table 1). The organic growth inhibitors which prevent dendritic growth in aqueous solutions appear to inhibit all growth in alcohol solutions. Most of the baths that were tested plated no silver whatsoever, and the only silver that was obtained resulted from the

addition of very small amounts of thiourea (less than .001 g in 30 ml). Even this deposit was thin and poorly adherent, mixed with a thick black deposit. None of these baths exhibited any improvement in deposit quality over the simple nitrate bath.

Before the nitrate bath was abandoned entirely, an attempt was made to increase the silver content that was possible by using a solvent that has stronger interaction with the  $\text{AgNO}_3$ . Propylene carbonate was chosen. The silver content was increased to .03 M. However, as was the case with the ethanol bath, any efforts to complex the silver from the nitrate resulted in the prevention of all silver deposition. Even after elaborate drying procedures were conducted on the propylene carbonate, only dark material continued to be deposited on the superconductor electrode.

The first successful smooth silver coatings were deposited when the silver ion source was switched from  $\text{AgNO}_3$  to compounds that more readily form complexes. Organic salts of silver were used: Both silver trifluoro-thiomethoxide and silver triflate were used as silver sources, and tetraethyl ammonium perchlorate and silver perchlorate were used as supporting electrolytes (see Table 2). The solubility of silver trifluoro-thiomethoxide was poor, even in propylene carbonate; the bath had less silver content than the nitrate-ethanol baths. However, the coating quality was good, and the switch to silver triflate which had a much higher solubility did not perceptibly improve the coating quality. Current densities were  $2 \text{ mA/cm}^2$ .

In order to get information on the effects of different bath compositions, a rough conductivity study was done. The voltage profiles for several electrolyte compositions are plotted in (Fig. 10). The

dominant trend was an increasing bath conductivity (decreasing voltage) over the period of operation of the bath. However, the baths with large concentrations of supporting electrolyte (silver perchlorate or TEAP) tended to have a constant conductivity with respect to time, indicating that the ions responsible for bath conductivity are not involved in single electrode reactions. The electrolyte with a high concentration of silver perchlorate had a very slightly increasing voltage, perhaps because of depletion of perchlorate at the anode (a dark film formed on the anode in this bath). The baths with larger concentrations of silver triflate had increasing conductivities. There may have been ion depletion near the electrode surface in these baths, leading to a higher concentration of charge carriers in the center of the bath where the platinum reference electrodes were located. In (Fig. 11), the voltages of the electrodes and the bath are plotted for a composition of 20 g/l silver triflate, 13 g/l silver perchlorate, and 23 g/l TEAP. The voltages for the anode and cathode each include the drop across several millimeters of bath, as the reference electrodes were not placed immediately next to the surfaces of the anode and cathode, and therefore the increase in bath conductivity will be reflected to some degree in these values. The anode voltage is seen to increase moderately, perhaps because of depletion near the surface of the anode, or because of film formation.

The most stable bath and electrode voltages were recorded for approximately equal concentrations of silver ion source and supporting electrolyte. Baths containing 20 g/l silver triflate, 13 g/l silver perchlorate, and 23 g/l TEAP had the best results of all the silver baths tested, and were used to deposit the silver coatings for final

characterization.

### 3.4 Silver Deposit Quality

Coatings obtained for all baths containing silver nitrate as the silver ion source were highly dendritic, with incomplete surface coverage (Fig. 12). Smoother coatings and fuller coverage were obtained with silver triflate and supporting electrolytes. In (Fig. 13), the silver deposit from 20 g/l silver triflate, 13 g/l silver perchlorate, and 23 g/l TEAP is shown. While some surface roughness and slightly dendritic formation can be seen, coverage is nearly complete and there is some evidence of silver penetration into the rough superconductor surface. The coating appeared to be quite adherent, as scraping with a spatula removed almost no material.

The contact resistance at 77K was approximately  $2.5 \text{ m}\Omega\text{cm}^2$ , which is slightly better than the value for aluminum. Again, the resistance decreased for increasing current densities.

### 4. Conclusions

Room temperature electrodeposition of aluminum with the superconductor as a substrate works well and does not affect the superconducting properties of the material. A bath consisting of aluminum chloride and lithium aluminum hydride in ether gives a smooth and continuous coating of aluminum, which adheres well after thermal cycling to 77K. The electroplated aluminum, although useful as a continuous, protective coating for the superconductor, has a contact

resistance that is too high for most applications. It must be kept in mind, however, that a finite interfacial resistance is needed to distribute the current density for the application of a parallel conductor to a flawed superconducting wire. In this case, depending on the geometry, the aluminum coating may have an appropriate interfacial resistance.

Silver electrodeposits, which are dendritic when deposited from alcohol-based baths, have improved structures when plated from organic salts of silver in propylene carbonate. The interfacial resistance of the coating is lower than that of the aluminum coating, but is still much higher than the contact resistance values that have been achieved for some high-vacuum processes<sup>4-6</sup>. The utility of the electrodeposited silver as an electrical contact would depend on the specific application; considerations would include the suitability of the coating method (see section 1.2). A bath with a composition of 20 g/l silver triflate, 13 g/l silver, and 23 g/l TEAP provided a silver coating with the best coverage and uniformity.

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Table 2

PROPYLENE CARBONATE BATH COMPOSITIONS  
grams/liter

Bath #	1	2	3	4	5	6	7	8	9
AgNO <sub>3</sub>	3.6	4.8	4.8	-	-	-	-	-	-
NaSCN	-	-	2.4	-	-	-	-	-	-
silver triflate (CF <sub>3</sub> SO <sub>3</sub> Ag)	-	-	-	6.9	29	20	13	20	56
silver perchlorate (AgClO <sub>4</sub> )	-	-	-	4.0	17	13	32	-	7.6
tetraethylammonium perchlorate ((C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NClO <sub>4</sub> )	-	-	-	-	-	23	-	46	-

FIGURE CAPTIONS

Fig. 1: Thermal expansion coefficients of aluminum and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  over the temperature range of 60 K to 300 K.

Fig. 2: Diagram showing current flow around a flaw in a superconducting wire, through a metal coating. The calculated interface current density as a function of the position relative to the superconductor flaw is plotted above.

Fig. 3: Plot of the engineered (desired) contact resistance as a function of the position relative to the superconductor flaw. This resistance is necessary to distribute the current away from the corner at the crack.

Fig. 4: Powder processing procedure steps, beginning from  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$ , and ending with the superconducting product ready for electrode formation.

Fig. 5: Front and side views of a fabricated superconductor electrode.

Fig. 6: Plating apparatus. Electrodes are attached and positioned with a machined teflon cap; electrical connections are made above the cap. Reference electrodes are platinum wires, shown encased in glass pipette tips (sealed with insulating epoxy) at the bath level.

Fig. 7: Electron micrographs of electrodeposited aluminum on the

superconductor (cross sections). The bakelite polishing mount is seen above the aluminum, and the superconductor is below. The dark areas between the bakelite and the aluminum are voids left during the mounting procedure. (NBS bath,  $40 \text{ mA/cm}^2$  plating current density)

Fig. 8: Electron micrograph of the aluminum/superconductor interface, showing the penetration of aluminum into the surface porosity of the superconductor. (NBS bath,  $40 \text{ mA/cm}^2$  plating current density)

Fig. 9: High magnification electron micrographs of the aluminum/superconductor interface. No reaction layer is visible, and pore penetration is seen at the 1 micron level. (NBS bath,  $40 \text{ mA/cm}^2$  plating current density)

Fig. 10: Voltages as a function of time in operation for propylene carbonate based baths. Compositions of baths 1-6 are listed below the graph. These are baths 4-9, respectively, in Table 2. ( $2.5 \text{ mA/cm}^2$  plating current density)

Fig. 11: Voltages of the bath, anode, cathode, and complete cell as a function of time in operation for bath with a composition of 20 g/l silver triflate, 13 g/l silver perchlorate, and 23 g/l TEAP. ( $2.5 \text{ mA/cm}^2$  plating current density)

Fig. 12: Electron micrograph of dendritic silver deposit of the superconductor. Several small spheroids of silver can be seen adhering to or slightly displaced from the superconductor substrate shown in the



lower part of the picture. The large dark circular region on the right is a void in the bakelite mount. (plated from  $\text{AgNO}_3$  in alcohol)

Fig. 13: Electron micrographs of improved silver deposit from a propylene carbonate based bath, composition of 20 g/l silver triflate, 13 g/l silver perchlorate, and 23 g/l TEAP. Again, voids can be seen in the mount material immediately above the silver coating. ( $2.5 \text{ mA/cm}^2$  plating current density)

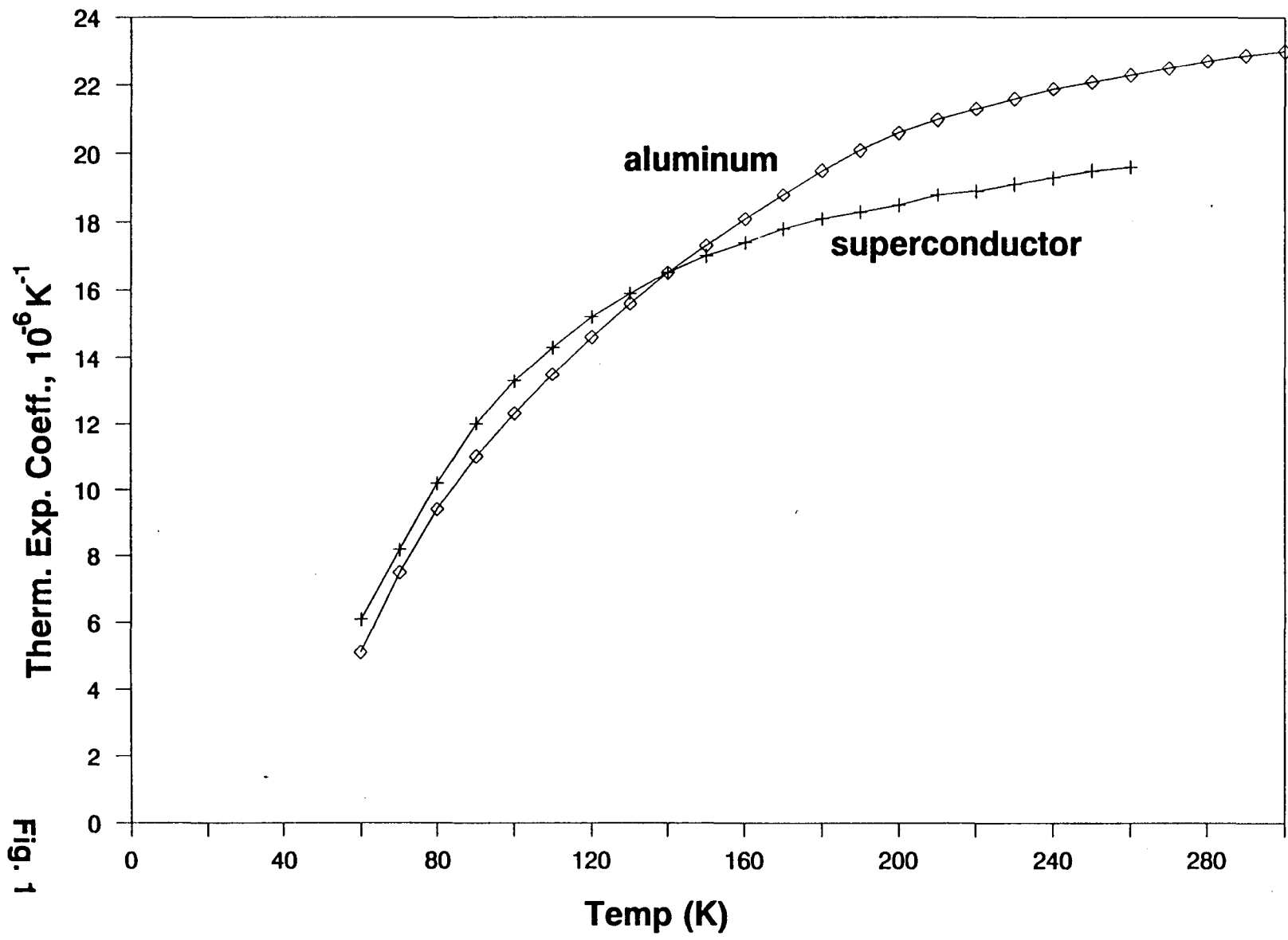


Fig. 1

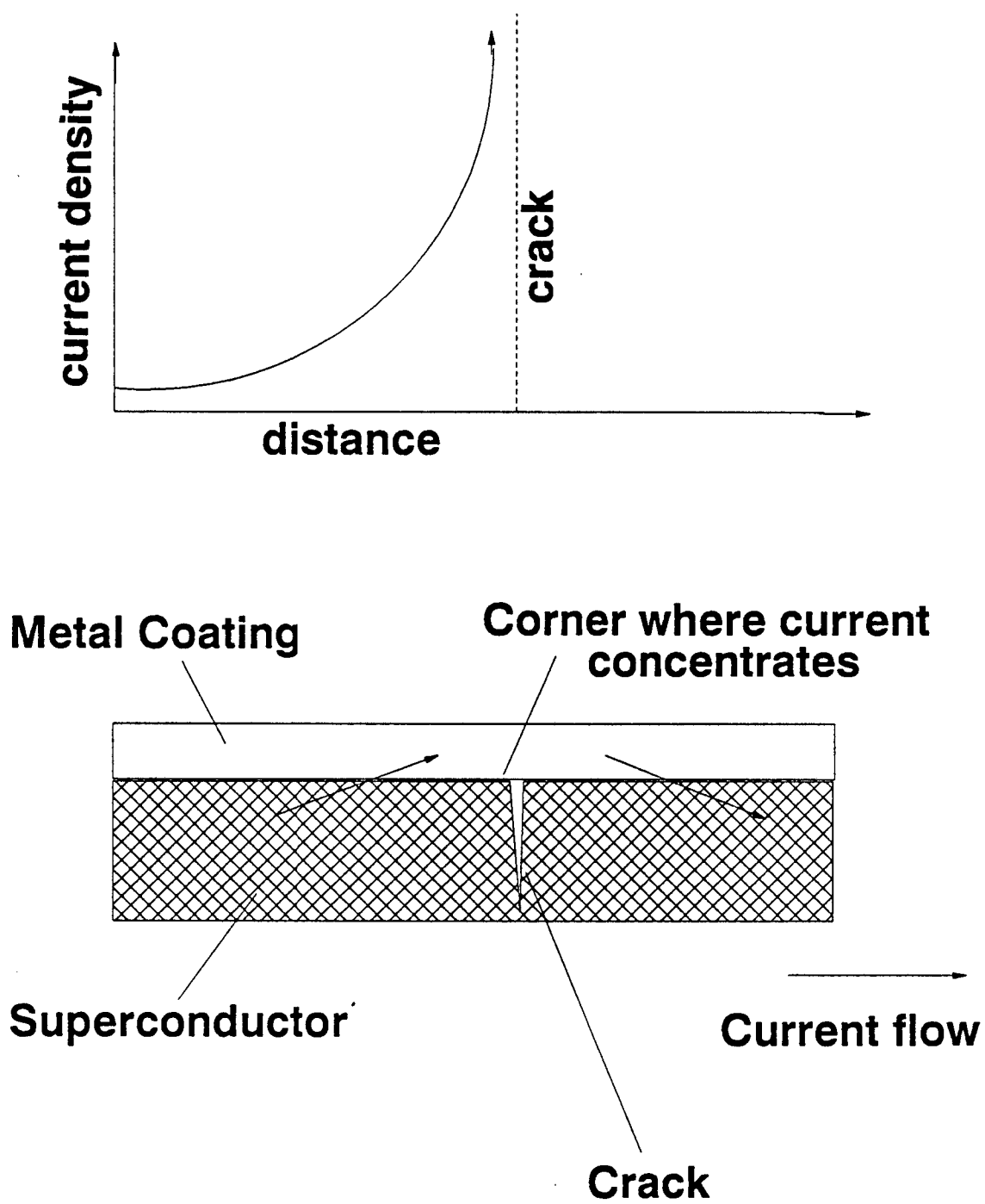
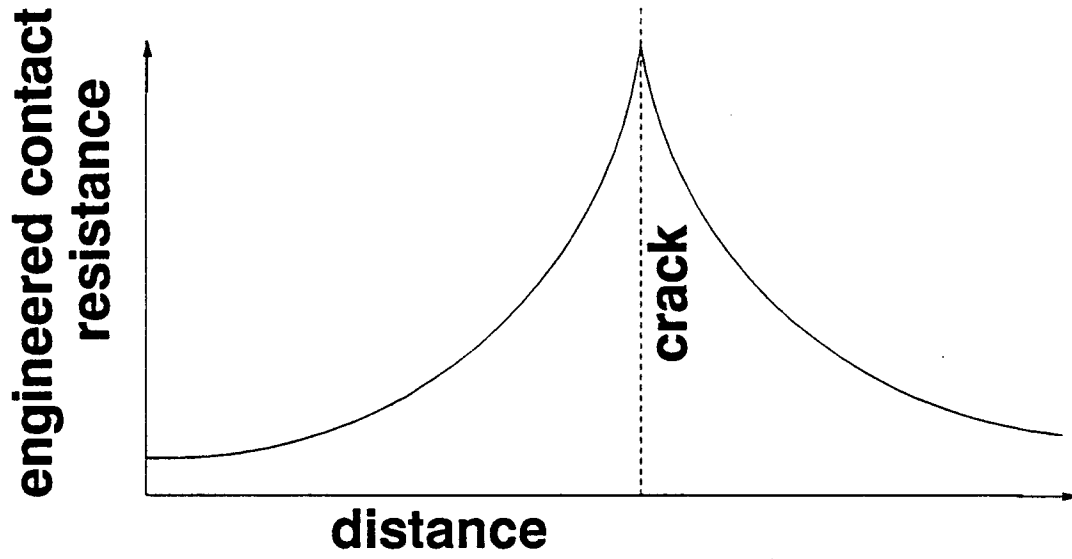
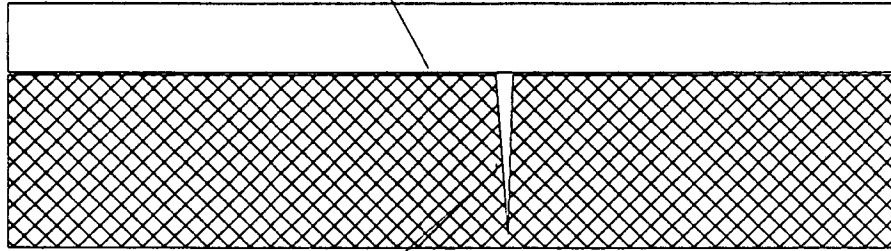


Fig. 2



**engineered interface**



**known location of crack**

**Fig. 3**

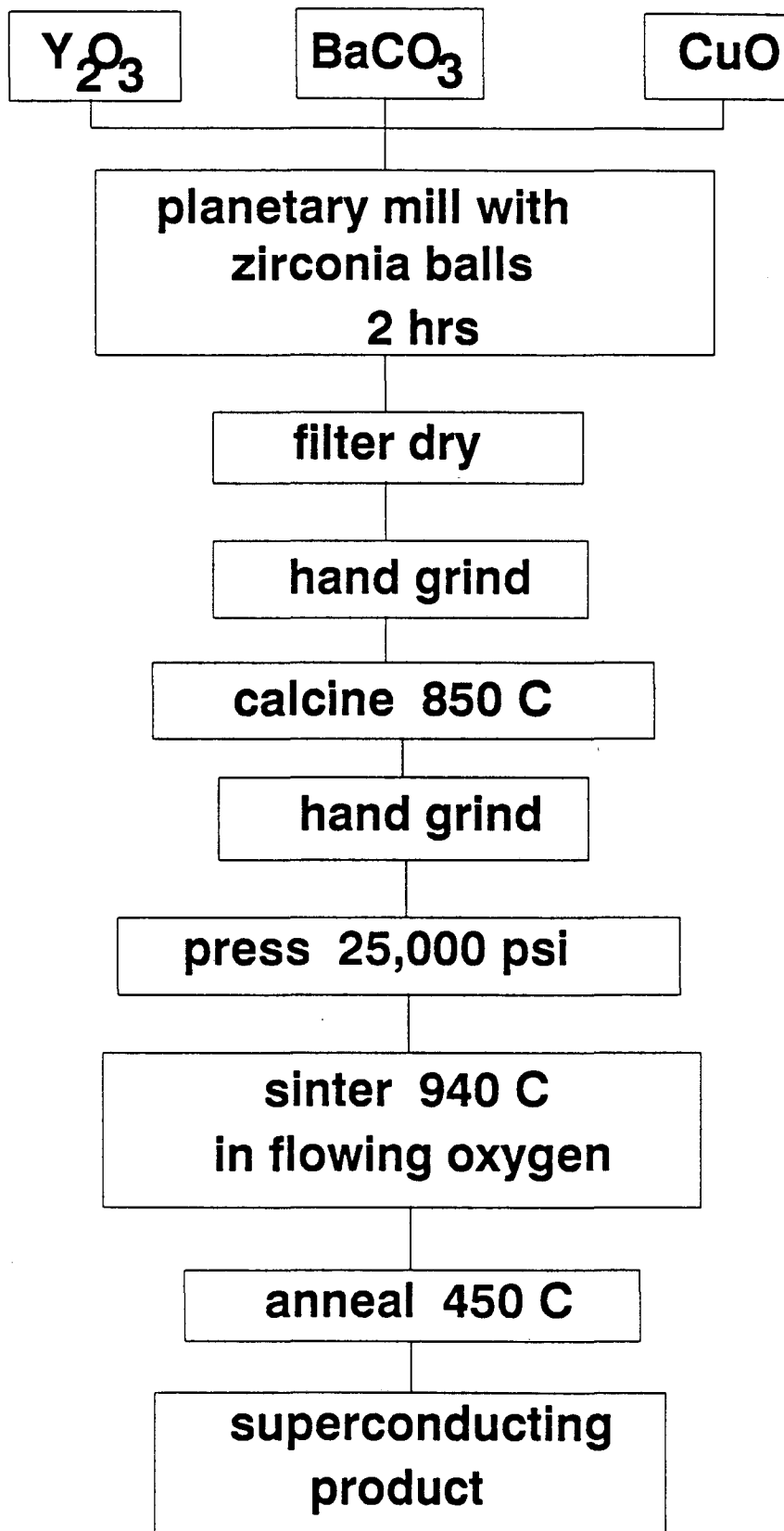


Fig. 4

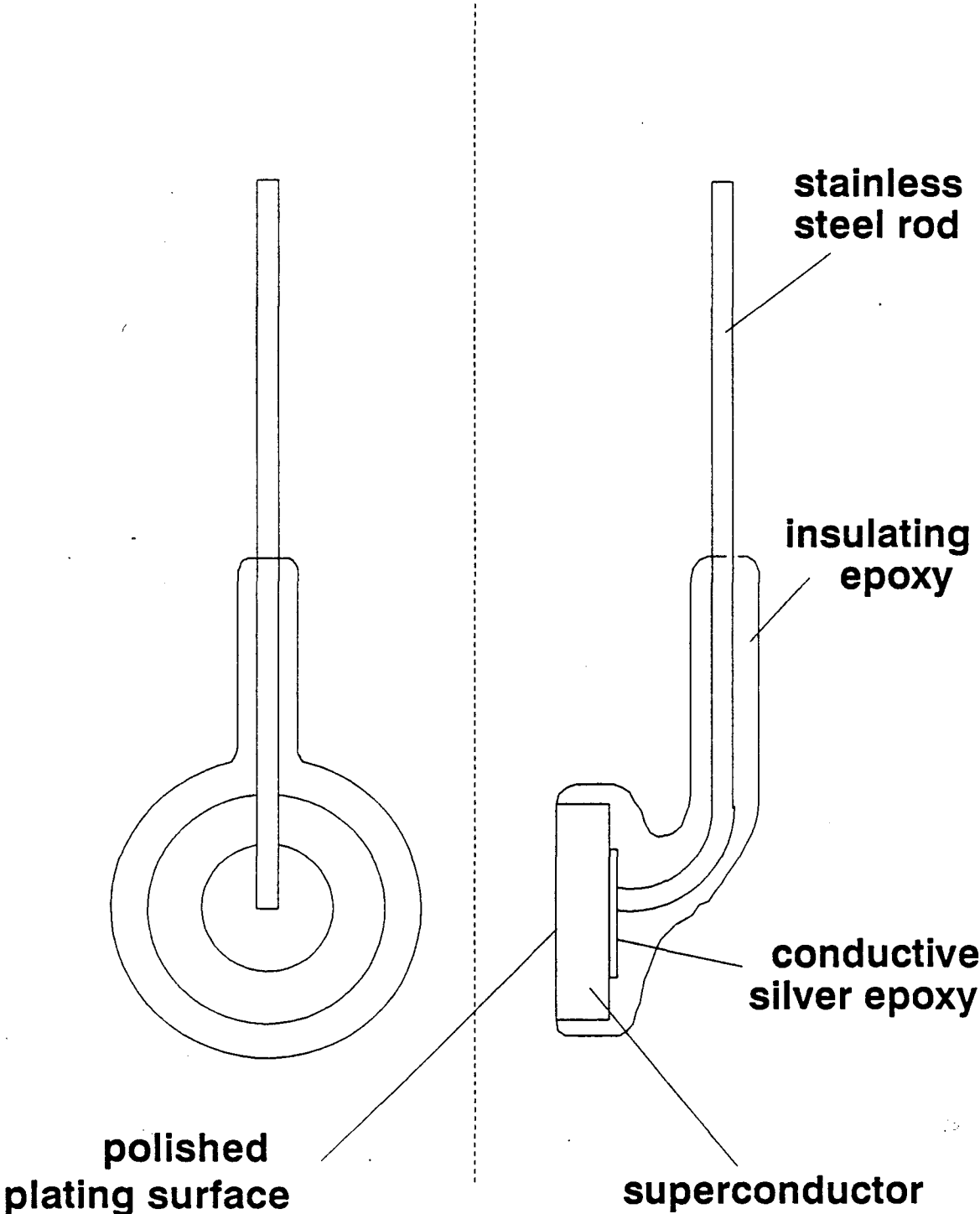


Fig. 5

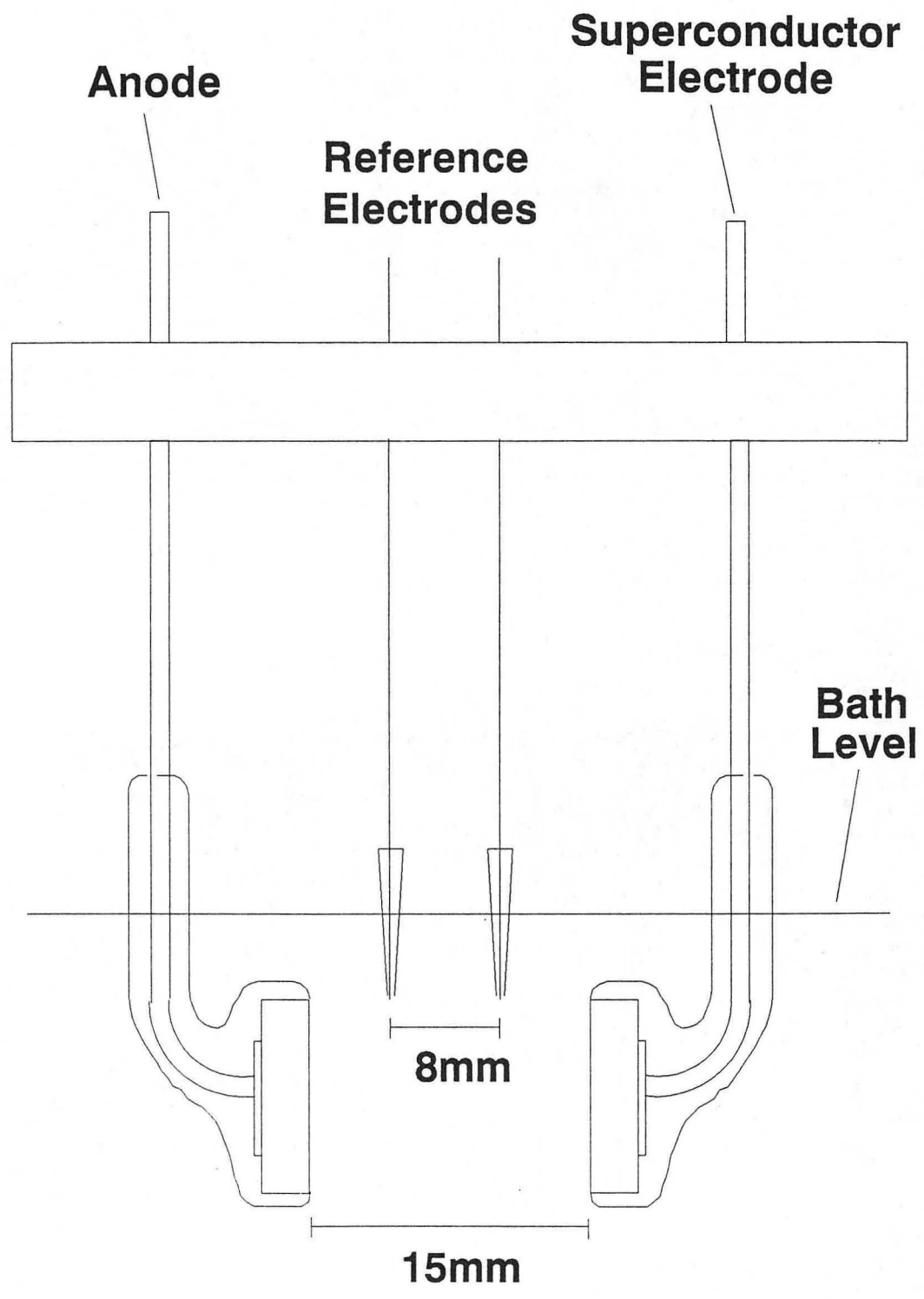
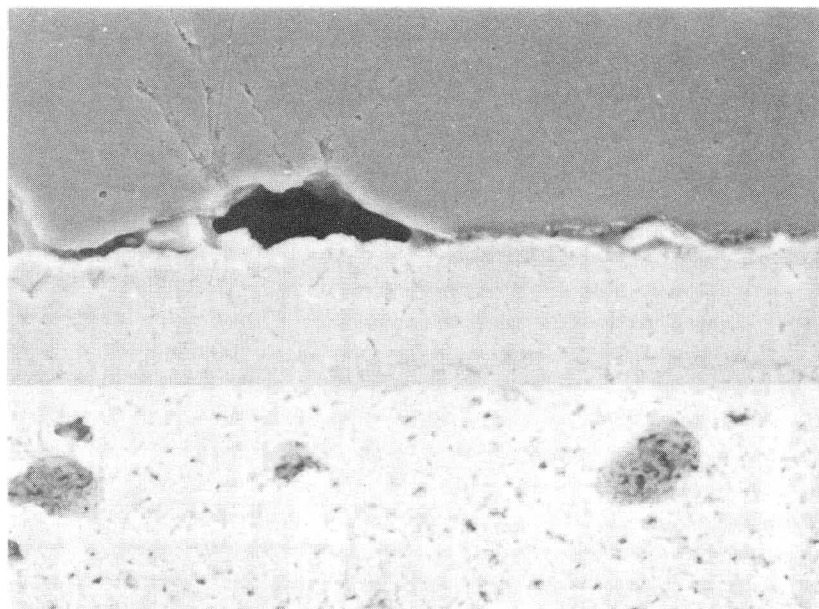


Fig. 6

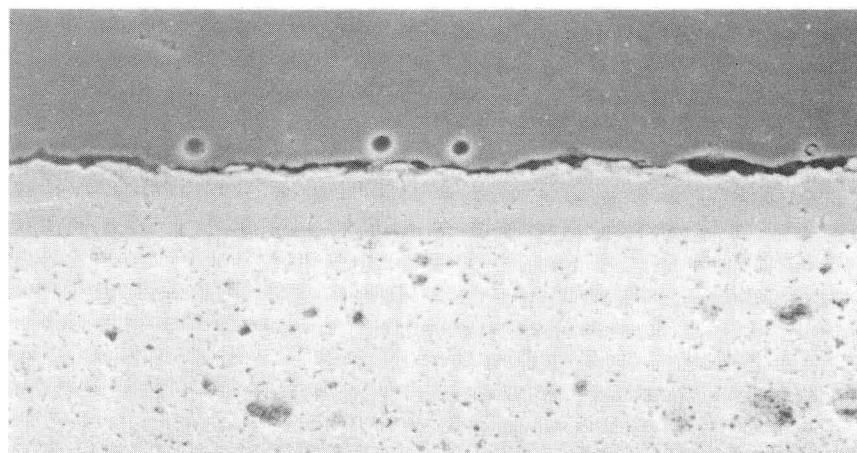


Mount

Aluminum

YBCO

27  $\mu\text{m}$

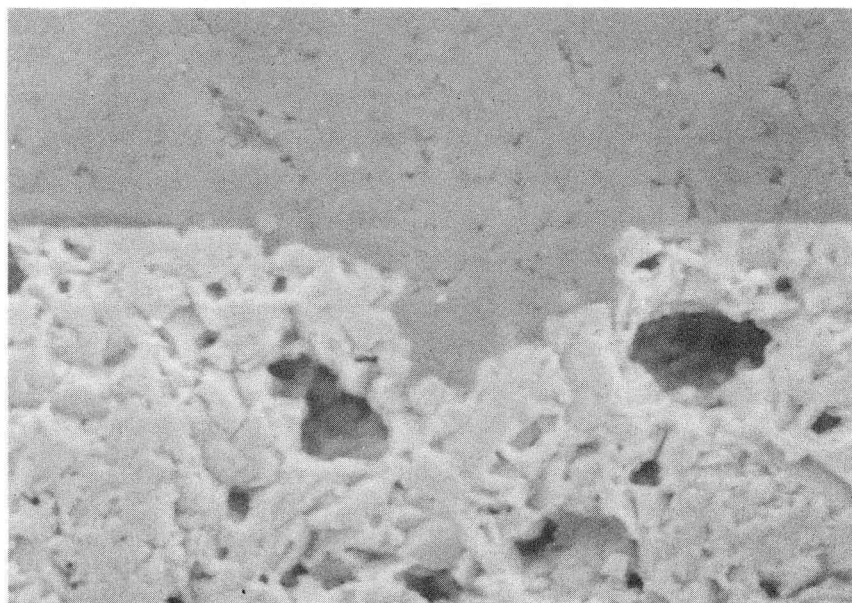


53  $\mu\text{m}$

XBB 890-9485

Fig. 7





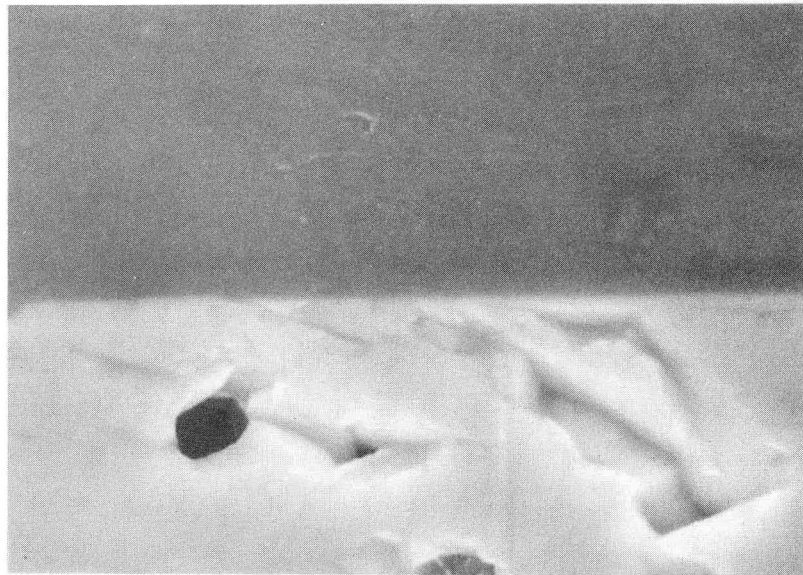
Aluminum

YBCO

8.9 $\mu$ m

XBB 890-9481

Fig. 8



Aluminum

YBCO

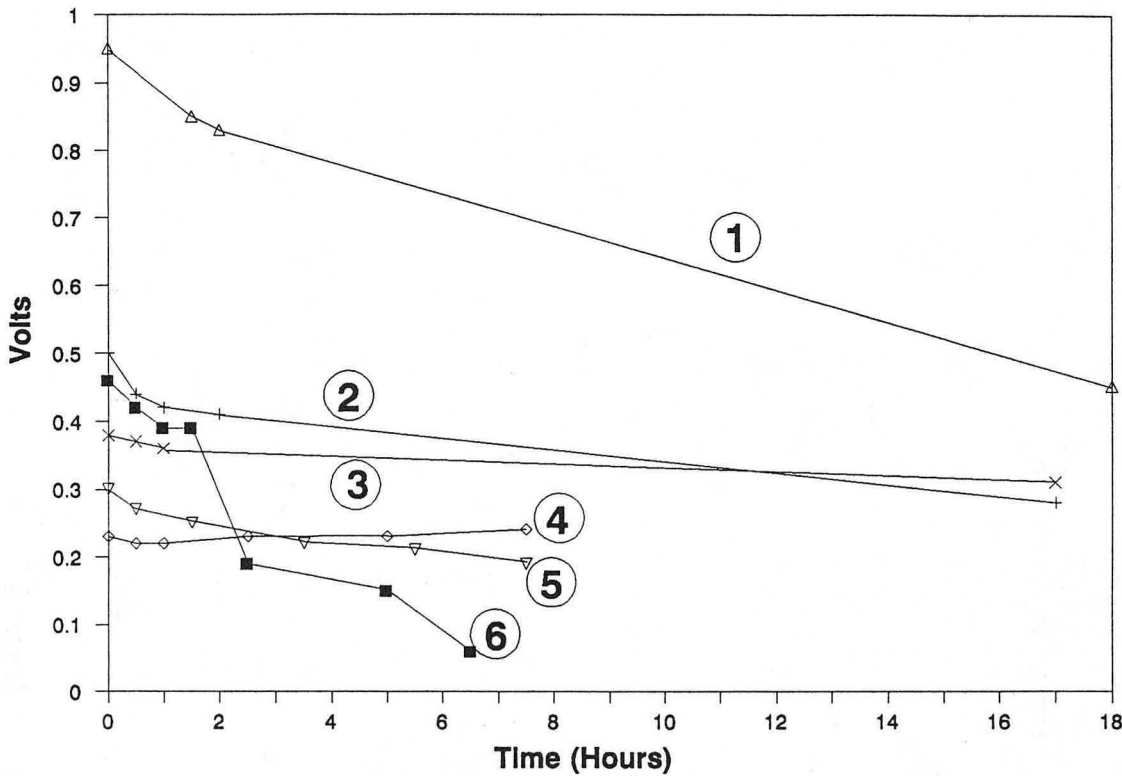
1.8μm



1.8μm

XBB 890-9484

Fig. 9



**Bath Compositions  
(grams/liter)**

Bath	Triflate	Perchlorate	TEAP
1	6.9	4.0	
2	24	17	
3	20	13	23
4	13	32	
5	20		46
6	56	7.6	

Fig. 10

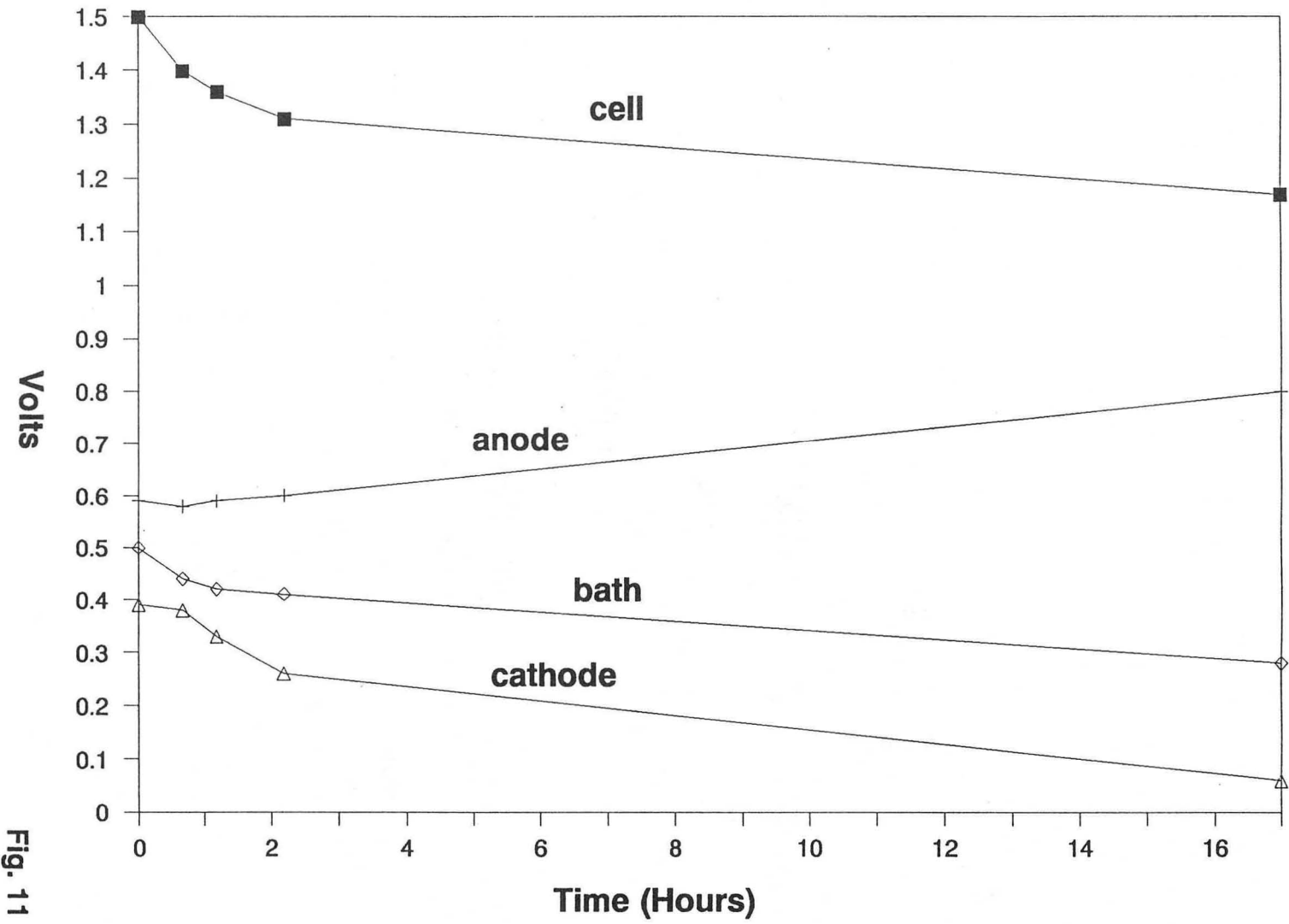
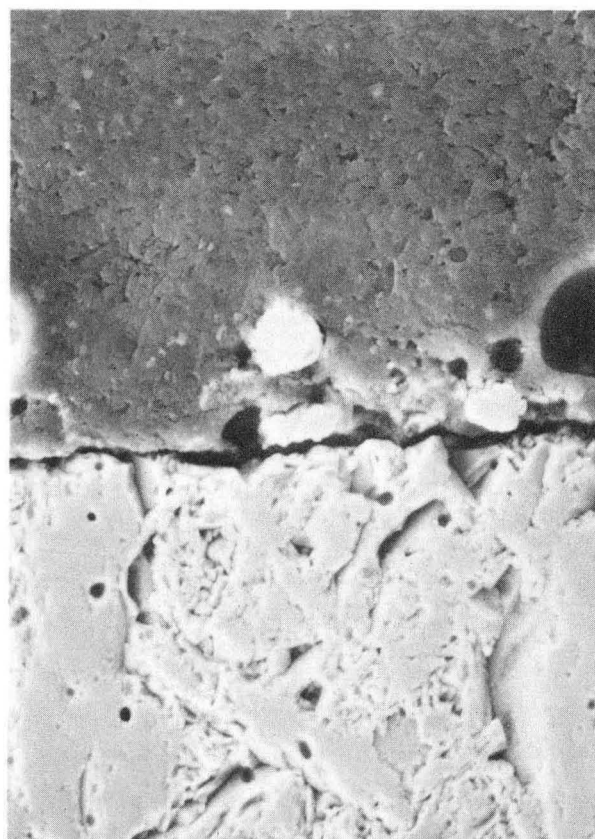


Fig. 11



Mount

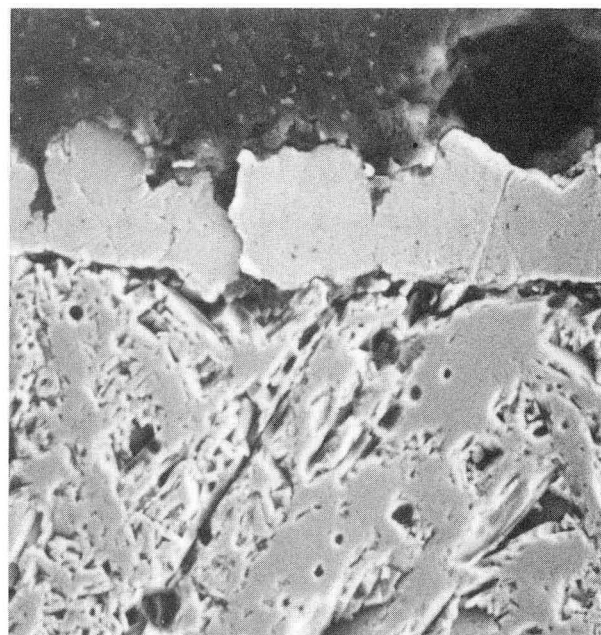
Silver

YBCO

12  $\mu\text{m}$

XBB 890-9482

Fig. 12



Mount

Silver

YBCO

12 μm

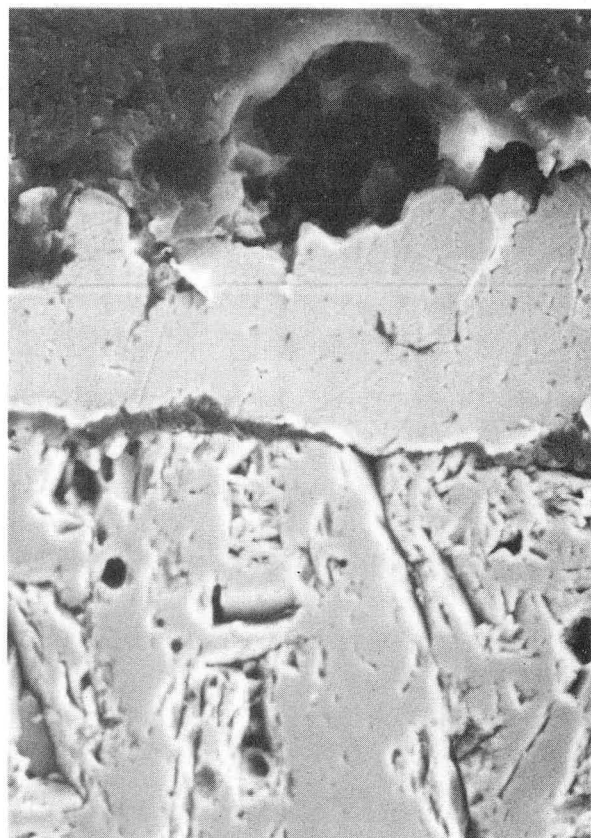


Fig. 13

8.1 μm

XBB 890-9483

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