

Recent Work on Lead-tin Superconducting Surfaces*

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For the last twenty years Stony Brook and several other low-frequency srf laboratories have used the same standard commercial electroplating technology to deposit thin lead and lead-tin superconducting layers on complex copper structures. While this Harstan plating technology worked well unfortunately it has become commercially obsolete, and consequently the essential proprietary organic additive, Shinol LF-3, is no longer available. A series of plating tests were recently carried out to find the most suitable Shinol replacement. Good results were obtained with both a high-acid fluoborate bath with a generic additive (gelatin + resorcinol) and a commercial methanesulfonic acid process (LeaRonol Solderon MHS-L).

1 Introduction

This report describes some recent development work on the electroplating baths used to create thin lead-tin superconducting surfaces on copper low-beta cavities. While various Stony Brook groups have made a number of improvements in “plating technology” over the years the basic workings of the plating bath itself (especially in regard to the somewhat mysterious Shinol LF-3 additive) were hardly ever considered. We were forced to address this aspect recently however, when it became clear that our last available stock of Shinol was no longer effective.

Various alternative plating baths were tested in a simple geometry, using a weighing technique to quantify throwing power. Promising test results were obtained for two quite different processes, one based on a generic additive and the other proprietary, and the first of these two baths has just been used to re-plate a set of split-loop resonators [1].

2 Background

The properties of electroplated lead as an rf superconductor have been reviewed by Delayen at a earlier workshop [2]. Besides Stony Brook, the current lead-copper srf community includes the heavy-ion linacs operating or under development at INFN-Legnaro, UW-Seattle, ANU-Canberra and TIFR-Bombay, and the Triton cyclotron project at Munich.

The history of the various Caltech and Stony Brook plating developments has been summarized in the last Stony Brook laboratory report [3]. The key improvement was the change about ten years ago from chemically polished pure lead to direct coatings of 1–2 micron lead-tin alloy.

3 Plating criteria

Some properties of the alloy coating that seem important to good resonator performance are:

- Good overall surface quality, with a compact crystal structure.
- An appropriate and uniform thickness
- An appropriate and uniform tin concentration
- Freedom from porosity and inclusions

High purity has not been listed because it is not clear that "purer is always better." Some impurities, such as co-deposited organic additives, seem to be acceptable while others, such as certain metals, may be very detrimental.

Overall surface quality can often be judged simply by close visual inspection or by a "wipe test" with a soft tissue. These observations should be made at some appropriate standard thickness, say 1.0, 1.5 or 2.0 microns. The best surface has a light grey or silver color and shows no mark when gently wiped. A good surface may or may not be highly reflective or "mirror-like", depending on the crystal structure of the copper substrate. A mechanically polished substrate will invariably give a matte or satin result while a one micron deposit on a chemically polished substrate can be almost as reflective as the substrate itself.

Thickness can be determined by weighing small samples, as described below, or by various standard analytical techniques such as RBS, SEM, XRF, etc. Some of these methods also give information on tin content and distribution and on the micro-coverage.

4 Plating chemistry

4.1 Fluoborate baths

Nearly all lead and lead/tin electroplating for srf applications to date has been based on fluoborate chemistry. In general a fluoborate plating bath contains the following components:

1. Lead metal as fluoborate, $Pb(BF_4)_2$
2. Tin metal as stannous fluoborate, $Sn(BF_4)_2$
3. Fluoboric acid, HBF_4
4. Boric acid, H_3BO_3
5. An organic additive
6. De-ionized water

The boric acid (4) is needed to stabilize the decomposition of fluoboric acid into hydrofluoric acid, which would result in the precipitation of lead fluoride [4]. The tin component is also somewhat unstable, in that the desirable stannous tin (Sn^{++}) slowly becomes oxidized to the inactive stannic form (Sn^{++++}).

The lead and tin fluoborates (1&2) are always obtained in the form of prepared concentrates which also contain sufficient boric acid and fluoboric acid to make a useful bath when combined with a suitable organic additive and DI water. Additional HBF_4 can be added as needed to lower pH and increase conductivity. Harstan lead and tin concentrates (and similar 50% concentrates from other manufacturers [5]) contain about 475 grams of lead or 325 grams of tin per liter of concentrate, respectively. The Harstan and equivalent fluoboric acid preparations are 48% concentration.

The composition of the standard Harstan bath used for many QWR and SRFQ platings [3] is: lead fluoborate concentrate 46 %; stannous fluoborate concentrate 1.0 %; fluoboric acid 3 %; Shinol LF-3M additive 2.0 %; DI water 48%. This recipe is essentially the same as the Caltech one [2] which was used for the original plating of the Stony Brook linac, except that the latter had no tin and no additional acid.

In general, a plating bath additive has several distinct functions, which may be effected by different chemical components. First, the additive must modify the electrical charge distribution near the surface of the copper cathode in such a way as to promote plating in low-current density (recessed) areas. The ability to thus achieve a uniform plating independent of the primary (unmodified) current distribution is called *throwing power*. Second, the additive must regulate the lead/tin crystal growth to promote a fine-grained surface structure without "treeing" in high current areas. Finally, in an alloy bath, the additive affects the ability to deposit tin.

When fresh, the Harstan proprietary additive Shinol LF-3 was quite effective in all these roles. However, due to a decrease in demand for commercial pure lead plating its manufac-

ture was discontinued approximately five years ago. For the same reason no alternative supplier has emerged. Some information is available on the chemical make-up of Shinol LF-3, but unfortunately one of the known ingredients is also no longer manufactured [6].

Of course throwing power and surface structure are also greatly influenced by the various plating parameters, especially plating rate (current density). For resonator plating a plating rate of 1 micron per hour (or even less) is entirely practical, while commercial plating rates would typically be 10–100 times faster. Uniformity is improved by plating slowly, but below 1 mA/cm² plating efficiency quickly diminishes. The advantages of low plating current can be achieved without loss of efficiency by millisecond pulse plating.

4.2 Methanesulfonate baths

Commercial technologies for lead-tin alloy plating are now oriented predominantly towards solder applications (printed circuits and chip leads). Fluoborate processes have largely been eliminated in favor of a less toxic and more stable alternative, methanesulfonic acid (MSA), which also offers much easier waste disposal. The leading company in this field, at least in the US, is LeaRonol [7]. Similar to the earlier Harstan fluoborate preparations, LeaRonol offers MSA lead and tin concentrates, an acid concentrate, and various specialized additives.

Some LeaRonol MSA baths for lead-tin resonator plating had in fact been briefly investigated at both Stony Brook and Oxford University about ten years ago. Throwing power was not nearly as good as with the Harstan Shinol LF-3 and this investigation was soon terminated. The Solderon additive used in these earlier studies was not the same as the Solderon MHS-L additive currently recommended for pure or nearly pure lead deposits. Recently we have learned that the Schlötter FF commercial process used to successfully plate the very large cavities for the Triton cyclotron at Munich is also based on MSA chemistry and additives similar to Solderon MHS-L.

5 Experimental Methods

5.1 Preliminary tests

The initial plating tests were made in a 267 ml "Hull cell." (In this industry-standard test geometry a 10 cm wide × 6 cm high cathode sheet (plated height = 5 cm) is fixed at a steep angle to the lead anode, to simulate a range of primary current densities.) Tests were made at both 1 Amp (20 mA/cm²) for 5–15 minutes and 0.1 Amp (2 mA/cm²) for 15 minutes. The higher rate is representative of commercial "low-speed" plating while the lower one is closer to (but still up to 10 x greater than) the current densities normally used for thin resonator coatings. Any reasonable bath should be able to give a satisfactory deposit over at least some of the cathode sheet at either current.

One Amp Hull cell tests with an existing bath used six months earlier to plate the final QWRs [3] invariably gave very dark and rough surfaces. Results with a bath freshly made up in the same way out of the same ingredients were even worse. Somewhat better but still not satisfactory platings were obtained after treating the made up bath with activated charcoal or plating at 0.1 Amps. These unusually poor results all pointed to decomposition of our final batch of Shinol, which had been purchased in 1992, as the source of the problem.

We next considered several alternative addition agents [4]. One the simplest was gelatin, which immediately gave an attractive silver-grey deposit over a wide current range. Based on this encouraging result we set up to test systematically a number of possible baths for appearance, plating efficiency and throwing power.

5.2 Beaker tests

The surface quality and throwing power of different baths were systematically compared by plating in a simple standard geometry. Anode and cathode strips each 6.0 cm wide were held parallel and ~3.0 cm apart in a 400 ml beaker. Each test was made with 300 ml of fresh solution which had been filtered through Watman 50 paper. The anode was a freshly-cleaned lead sheet,

while the cathode consisted of a 25-micron thick high-purity copper foil wrapped tightly around the copper strip. The cathode was cleaned before use by immersion in Shipley Neutraceutical and rinsed thoroughly with DI water.

Each of the candidate solutions was tested at five complementary current and time values ranging from 25 mA for 60 min to 200 mA for 7.5 min. Since the total plated area (front + back) was $\sim 100 \text{ cm}^2$ the corresponding current densities ranged from 0.25 to 2.0 mA/cm² and the average thickness should have been slightly less than 1.0 micron.

The analysis procedure is designed to measure the thickness of a deposit without knowing the exact area of the sample. Two small samples are cut from the center of the "front" and "back" plated foils. Each sample is carefully weighed on a microbalance, then chemically stripped of all lead, rinsed and dried, and weighed again. The deposit thickness in microns is then given by

$$F \text{ or } B = 22 \times \left(\frac{W(\text{lead} + \text{copper})}{W(\text{copper})} - 1 \right).$$

The scaling factor (22) was determined by weighing several copper samples with accurately measured areas.

The total deposit ($F + B$) is proportional to plating efficiency while B/F is a measure of throwing power. Uncertainties due to other effects (variations of plating time and current, weighing errors, total plated area, loss of copper during stripping) total about $\pm 5\%$.

6 Results

Four different plating chemistries were tested to varying degrees in the course of this work:

1. A bath similar to the traditional Harstan one except that the additive is Atotech FGR, a commercial peptone.
2. A fluoborate bath based on a different type of Shinol, Shinol TLM-15, which unlike Shinol LF-3 is still available from a secondary supplier [5].

3. A commercial bath based on methanesulfonic acid rather than fluoborates (see Section 4.2 above). Like the original Harstan process the Solderon MHS-L additive is proprietary.
4. A high-acid fluoborate bath based on the readily available generic additives purified gelatine (from swine skin) and resorcinol ($\text{C}_6\text{H}_4\text{-1,3-(OH)}_2$), as proposed in Ref. [4].

Bath (1) was very dark and had a very foul odor, even worse than the traditional Shinol baths. The throwing power was so poor that copper showed through lead on the back side of the cathode. This process was quickly rejected.

Bath (2) gave reasonably good results, but the additive tended to separate out of the bath into an oily surface film very quickly after current was applied. Also, the current supplier [5] recommends TLM-15 only for solder baths with nearly equal lead and tin.

Bath (3) was only very briefly investigated so far due to time constraints, but it seems very promising. The components of the one liter test bath were: Solderon acid 350 ml; Solderon lead 33 ml; Solderon tin 2.5 ml, Solderon MHS-L additive 100 ml. The bath is clear with a slight amber color and not much odor. Deposits were very metallic looking, similar to or better than the best bath of type 4. The throwing power was not measured but was estimated from stripping times to be approximately equivalent to a B/F ratio of 50% or better. Clearly this new chemistry merits further investigation, for example to optimize throwing power at low plating currents and to test the idea that additive concentrations can be greatly reduced by millisecond pulse plating [8].

Bath (4) received the most attention. In a series of tests the acid and metal content was varied over a wide range. Results did not seem to be very sensitive to the exact gelatin and resorcinol concentrations, so these were fixed at 1.0 and 0.5 grams per liter of bath, respectively. In striking contrast to Shinol and peptone baths the gelatin+resorcinol bath is water clear after filtering and has almost no odor, making it easy to observe the evolving deposit *in situ*. Best throwing power and appearance was obtained with the following amounts of metal and acid

per liter of bath: lead fluoborate concentrate 95 ml; tin fluoborate concentrate 1.5 ml; fluoboric acid 250 ml. This is much less metal, but much higher acid, than contained in the traditional Harstan baths.

The following table summarizes the beaker test results for this optimum gelatin+resorcinol bath. The first row shows the plating rate in mA per cm² of total area; the second row, *efficiency*, compares the total deposit $F + B$ to that expected from Faraday's law; and the third row, *uniformity*, gives the B/F ratio. It is apparent that the plating efficiency is close to 100% across nearly the whole current range, except perhaps at the slowest rate. On the other hand the uniformity clearly diminishes with increasing plating rate. Based on these data and similar results for slightly different acid and metal proportions, a good current density for the gelatin+resorcinol bath is about 0.5 mA/cm².

Rate	0.25	0.50	1.0	1.5	2.0
Efficiency	85%	95%	104%	96%	102%
Uniformity	105%	90%	85%	75%	67%

It should be noted that nearly identical efficiency and uniformity trends were obtained in similar tests several years ago with the standard Shinol LF-3 bath. Based on those tests the current density for the QWR platings [3] was set at 0.26 mA/cm².

Various "front" and "back" samples plated with the above optimized gelatin+resorcinol bath were analyzed by SEM, XRF and RBS to determine the surface thickness and microstructure and the tin concentration and distribution. As expected, the tin fraction was in the 2-5 at% range considered optimum for enhanced rf superconductivity. In the SEM the plated deposit had a very level surface and a fine grain structure, with no detectable voids.

7 Conclusions

We have identified two promising alternatives to the now-obsolete traditional Harstan/Shinol process for resonator plating. Further testing will be needed to optimize plating performance,

to determine long-term stability, and to reveal any possible differences in superconducting performance.

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