# RE-PLATING THE ANU LINAC

Nikolai R. Lobanov[†], David C. Weisser, Department of Nuclear Physics
Nicholas J. Welham, Department of Applied Mathematics,
Research School of Physical Sciences and Engineering,
The Australian National University, Canberra ACT 0200 AUSTRALIA

## Abstract

The nine split loop resonators, SLRs, for the ANU LINAC have been re-plated with 96%Pb, 4%Sn using Methyl Sulfonic Acid, MSA, chemistry. The resonators were originally plated with pure Pb using fluoborate technology. The recent upgrades are described for the lead plating process and the repair of cracks in electron-beam welds. An average acceleration field of 3.6 MV/m has been achieved on-line.

## 1 INTRODUCTION

Lead plating has been recognized as an appropriate technique at low frequency providing only slightly poorer performance (BCS losses) than Nb super-conducting layers. Lead plating provides fast moderate results with modest equipment at relatively low cost. In order to prevent lead oxidation and contamination during post-plating treatment, lead-tin was adopted for SUNY QWRs and for the Munich cyclotron. In spite of the reported difficulties in controlling the tin concentration and lower RRR value compared pure lead (50 for pure lead, 24 for 2% tin-lead), both laboratories demonstrated remarkable results. The "traditional" resonator plating chemistry is no longer commercially available, as Shinol, the lead additive, and Pb fluoborate have become obsolete for economic and environmental reasons. SUNY re-plated six high-beta SLRs with 2 microns of Pb-Sn alloy using a modern, commercial, methyl-sulfonate process (LeaRonal Solderon MHS-L) and a simple open-air procedure [1]. This proven success motivated ANU to adopt MSA chemistry and to re-plate the first SLR in November 1998 followed by re-plating the entire ANU Linac. This will increase the booster energy gain with the same number of resonators by up to 100%. Lead plating is preferred for substrates of complex geometry like SLRs because of difficulties in sputter coating such shapes with Nb.

## 2 CRACK REPAIR AND SURFACE TREATMENT

Four of the nine re-plated resonators were found to have cracks in the cosmetic electron beam welds at the base of the stem that supports the split ring. Solder, 60%Sn, 40%Pb with a melting temperature of 180°C, was used to repair the cracks. The cracks were in the circular grooves and were about 0.5 mm wide and up to 40 mm

---

[†]Nikolai.Lobanov@anu.edu.au

long. The solder wetted and filled the groove satisfactorily with a small dihedral angle resulting in a bright, smooth surface with no pinholes. Lead could not be plated directly onto the solder because the MSA plating solution vigorously attacked the tin-lead solder. Brush electroplating layers of nickel and then copper over the solder solved the problem. Performance of the re-plated resonators, throughout the field range up to more than 200 G, was quite similar to that of lead plated SLRs with no cracks. Thus the method provided a convenient and economical means of crack repair for large RF currents. A detailed account of process is described in [2].

The next preparation step, the most important step in coating procedures, is the careful surface treatment of the copper substrate. Surface preparation of the SLRs comprised several steps. First, all cavities and tuner plates were stripped of lead in LSTRIP2000, which works well for both lead and lead-tin coatings. RF surfaces were then thoroughly hand lapped with non-embedding garnet with grit sizes from 5 microns to 1 micron. The best finish on the tuner plates should be on the surfaces exposed to high electric field within 10 cm of the beam hole. On the SLRs, the best finish is needed on the loop arms, where the current is a maximum and on the drift tubes, where the electric field is high. SEM analysis of samples polished in the same way, revealed up to $4 \times 10^4$ particles per cm$^2$ embedded in the copper surface. Those included aluminium oxide and silica particles up to 5 microns in size. Abrasive inclusions will create micro-areas in the lead-tin film with poor thermal contact with the copper substrate. Nevertheless, we rejected the option of using a chemical etch, which can produce a defect-free substrate, because of the danger that it might break through the thin cosmetic electron beam weld exposing more cracks. Chemical etching was also not compatible with solder repaired resonators.

Non-RF surfaces were hand lapped with 1200 grit paper and 5 micron abrasive only. Special attention was given to cleaning the lead gasket groove, edges and recess holes. Since our SLRs have a sharp corner at the bottom of the flange groove, all traces of contaminants and rolled copper from this area had to be removed with a sharp file.

Polishing was followed by a thorough rinse in alcohol with care given to difficult areas including holes, grooves and recesses. The parts were then soaked for 5 to 10 minutes in an alcohol bath prior to vapour degreasing, Figure 1a. After three immersions into the vapour degreaser, Figure 1b, the job was cooled to room temperature.
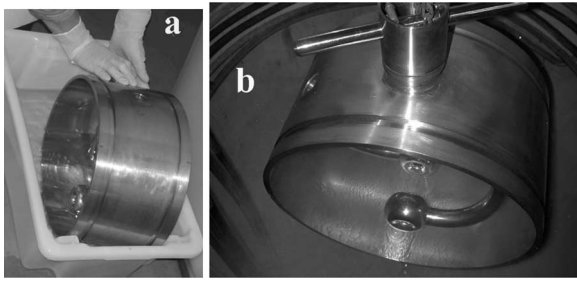
Figure 1: Surface cleaning SLR: a) soaking in alcohol bath prior vapour degreasing; b) vapour degreasing.

Once cooled, the part was soaked and washed 2 or 3 times in a clean alcohol bath using DURAX wipers. This was followed by soaking in DECON-90 for 5 minutes at 40°C followed by DIW/HPR. The next step was to soak in NEUTRACLEAN-7 for 5 to 7 minutes at 40 to 50°C then hot water and room temperature DIW/HPR. Finally, soaking in 5% citric acid for 5 minutes and rinsing in DIW/HPR passivated the resonator parts.

No materials other than copper were allowed to be in contact with copper plating solution. The phosphorus deoxidized copper anode sheets were processed in DECON/Neutraclean/Citric before installing them into the plating bath. Pre-degreased lead anodes were lead stripped in LSTRIP2000 following by soaking in alcohol before assembling and installation. Both copper and lead plating baths were operated with dummy substrates at current density higher than for plating for twenty minutes before the resonator plating commenced.

The entire surface of each resonator was electroplated with 0.5 microns of copper, Figure 2a. The SLR was immersed in the copper sulfate bath and the current ramped to either 8 A (tuner plate) or 16 A (SLR) for 7 minutes and then rinsed with DIW. Any surface defects in non-critical locations, such as brownish patches, were removed with 1200 grit paper immediately followed by HPR. The job was then soaked in 5% citric acid for 1 to 2 minutes followed by DIW/HPR and immersed into the MSA bath. The current was ramped to 17 A (tuner plate) or 35 A (SLR), Figure 2b. It was essential to circulate the MSA solution across the inner top part of the resonator can to achieve good plating quality, Figure 2c. No circulation was required for tuner plates. After plating, the pieces were immersion rinsed twice in DIW, the second bath containing ~0.015% ammonia. Nitrogen was bubbled through both rinse baths for a few hours in advance to reduce dissolved oxygen. As the plating solution aged, some staining appeared on the freshly plated surface. This could be removed after rinsing by immersion as rapidly as possible in an alcohol bath. The alcohol quickly replaced the water substantially reducing the drying time. Irrespective if alcohol was used or not, drying was hastened by vigorous blowing with nitrogen gas-guns, which were directed mainly at the critical RF surfaces. As soon as the part was dry it could be stored in a nitrogen atmosphere for many days without any degradation of the lead surface. Intriguingly, a visible improvement in the

overall appearance of the lead surface occurred within 24 hours, an effect that will be discussed in the next section.
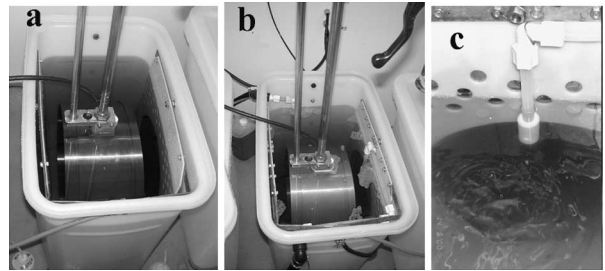


Figure 2: Copper/Lead plating SLRs: a) copper plating bath; b) lead plating bath; c) circulation of the MSA plating solution.

The re-plated split loop resonator R#306, immediately after drying, is shown in Figure 3.



Figure 3: SLR R#306 re-plated in May 2001.

## 3 POST-PLATING STAIN EXAMINATION

White and dark gray stains were noted after lead plating of samples and SLRs on some occasions. In order to understand the composition and cause of the stains, several samples were deliberately allowed to stain by leaving them to dry under various conditions. These were examined by X-ray diffraction, XRD. XRD spectra of four different samples are shown in Figure 4. Spectra are on a log scale and offset for clarity. Samples pb12 and pb14 had normal gas nitrogen drying followed by storage in nitrogen atmosphere, (pb14) and in vacuum, (pb12). Neither developed any stain. Sample pb36 was allowed to dry naturally in air after a final alcohol rinse. Sample pb19 was left to dry in air after a final rinse in DIW. Both pb19 and pb36 were stored in nitrogen atmosphere and both developed dull white stains. We suggest that such

stains may be produced on resonator surfaces under the last puddle of drying water.

The spectra shown in Figure 4 indicate that the stains were primarily due to orthorhombic PbO. There are also some peaks for a hydrated version of this oxide, $PbO.0.33H_2O$.
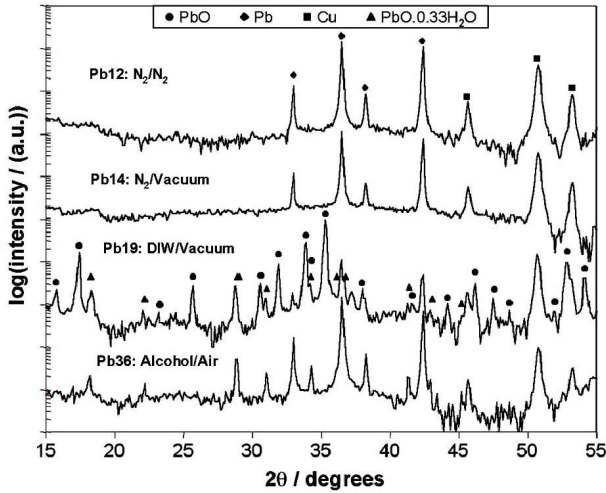


Figure 4: XRD spectra of lead plated copper samples for various drying/storage conditions: pb12: gas $N_2$ dried and stored in gas $N_2$; pb14: gas $N_2$ dried and stored in vacuum; pb19: air-dried after DIW rinse and pb36: air-dried after alcohol rinse.

We examined the surface layer to see if there were changes in the composition with depth by grazing incidence XRD [3]. Using a grazing angle enhances signals from the upper part of the layer and, as the angle increases, the contribution from this layer reduces. There was little change with angle in the XRD traces for sample pb19, which indicates that the oxide layer extended almost to the Pb-Cu interface. Copper and lead only became evident at a depth of 1.20μm (lead more so than copper) suggesting that most of the Pb in the system was present as PbO throughout the layer.

Similarly in sample pb36, the hydrated oxide, $PbO.0.33H_2O$, was present throughout the layer; there was no evidence for PbO on the surface. Since samples pb12 and pb14 did not reveal of any oxide on the surface, it could be surmised that the depth of the oxide layer is less than a few tens of nm, the approximate depth resolution in the GI XRD technique.

The phase diagram for lead in the presence of $CO_2$ and oxygen is shown in Figure 5. In the presence of $CO_2$ the formation of carbonate phases not is predicted to occur under atmospheric conditions (log $pO_2$ = -0.7 and log $pCO_2$ = -3.48) and this is confirmed by XRD. Similar calculations for lead in the presence of oxygen and water showed that $Pb(OH)_2$ is only stable under extremely high water partial pressures and, were it present, it would be expected to decompose. Interestingly, the stable form of lead oxide under atmospheric conditions (log $pO_2$ = -0.7) is $PbO_2$, this oxide is not found in nature suggesting that it

either difficult to form or is unstable in air. The other lead oxides $Pb_3O_4$ and PbO are both found in nature indicating stability over geological time; $Pb_3O_4$ is called minium and PbO is either litharge or massicot. The lead oxide found here is the white orthorhombic form (massicot). It is a high temperature form, stable above 500°C, indicating that transformations within the lead-oxygen system are kinetically slow and once a phase is formed it is likely to remain.
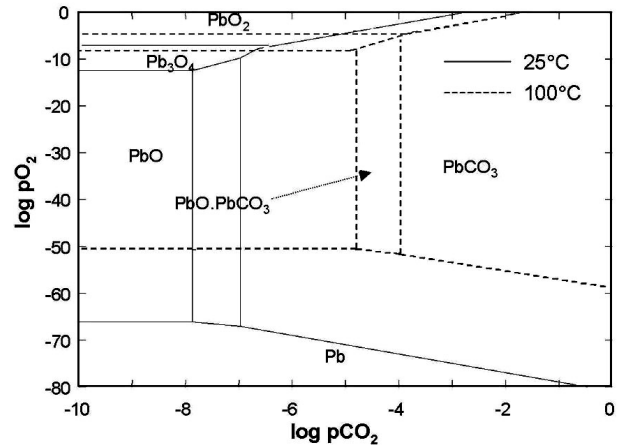


Figure 5: Phase diagram of lead in the presence of $CO_2$ and oxygen at 25 and 100°C

Once the sample was installed into the vacuum system, the partial pressures would decrease substantially. At $10^{-8}$ Torr, the partial pressure of oxygen and $CO_2$ (assuming the relative composition of the chamber is the same as air) becomes $10^{-8.6}$ and $10^{-11.5}$ respectively, the water content would be substantially lower than these. These conditions are sufficient for any carbonate or hydroxide to decompose to oxide and $PbO_2$ to reduce to $Pb_3O_4$, but not enough for the formation of PbO or elemental lead, which requires a substantially lower partial pressure of oxygen. Baking the system at 100°C under vacuum could result in the reduction of $Pb_3O_4$ to PbO, but no further. We conclude that the stain, which diminished over 24 hours, was probably a carbonate or hydroxide.

The XRD analysis shows that the formation of an oxide layer on a freshly plated lead film depends on exposure to a wet atmosphere. This exposure clearly has to be minimized by a rapid drying procedure. Previous results indicate that all the samples from the lead cavities had a surface [16]O concentration that would correspond to a PbO thickness of about 10 nm. The loss tangent of PbO oxide layer was to be estimated below *10^-5* showing that dielectric losses do not make a major contribution to $R_{res}$. The same trend was observed for residual loss from oxides in Nb cavities. Systematic experiments with oxide-free cavities placed a lower limit of 1-2 nΩ for the oxide contribution [4]. Due to a procedural failure during the drying operation, two out of nine re-plated SLRs developed areas of grey stains on the arms and outer walls. Discoloration indicated presence of a thick oxide layer of

few tens of nm. However, no difference in the resonators performance was observed.

## 4 CAVITIES ON-LINE PERFORMANCE

Q values were measured by the decremental method. At present, the six SLRs in two ASI module cryostats, have an average accelerating field, $E_a$ of 3.6 MV/m at 6 Watts. The best resonator achieved 3.8 MV/m at 6 W as inferred from the energy gain of a 6$^+$ $^{12}$C beam, Figure 6. $E_a$ is defined as in [5], $\Delta E/q= E_a L \cos(18°)T(\beta,)$ where $\Delta E/q$ is the actual energy gain per unit charge, $L$ =22.1 cm is the active length of the SLR, *-18°* is the operating phase and $T(\beta)=1$ for an ion with optimum velocity $\beta=0.10$.

The higher accelerating field of re-plated SLRs challenged the RF stabilization system. The required tuning power $P{\sim}U{\sim}E_a^2$ had to be increased by $(3.6/1.7)^2$= 4.5 for the same operational bandwidth. As well, the static radiation pressure frequency shift, $\Delta f_{rad}=-100E_a^2$, also increased by a factor of 4.5, that is a radiation pressure shift of 1.3 kHz at 3.6 MV/m. Thus, substantial mechanical frequency tuning is necessary if experimenters require a change of $E_a$.
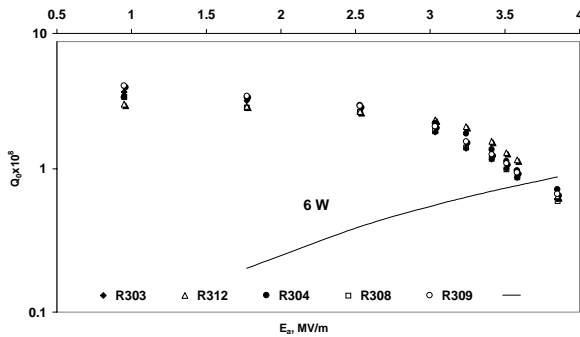


Figure 6: Typical Q vs. $E_a$ curves of the five re-plated SLRs recently installed in ANU LINAC. Line for $Q_0$ vs $E_a$ at 6 W is shown.

The LINAC will be able to provide an energy gain of ~ 9 MeV/q for beta 0.1 beams when the next 6 resonators are re-plated. The main advantages of lead plating technology are reliability, simple surface preparation, the possibility of solder repair of the substrate and an inexpensive process.

The maximum accelerating field so far achieved is 3.6 to 3.8 MV/m. Could this be the magnetic field limit? Lead is a Type I superconductor with $H_c(0)$=800 Oe. In *RF* conditions, there is tendency for the metastable superconducting state to persist up to $H_{sh}$. For lead, $H_{sh}$=1.5$H_c$=1200 Oe. For the SLR geometry, $H_c/E_{acc}$=110 Oe/MV/m implying a magnetic field of less than 400 Oe at 3.8 MV/m, well below the 1200 Oe limit. Since the peak surface electric field, $E_p$= 5.5$E_{acc}$, $E_p$ = 20.9 MV/m, the electric rather than the magnetic field is the one that more likely limits the performance of the SLRs. Some possible sources limiting performance are discussed below.

### 4.1 Surface condition

A mechanically polished surface is adequate for 3.6 MV/m, but may be what limits performance at higher field. Up to $10^6$ particles per cm$^2$ was found after samples were hand polished with 1200 grit paper. In contrast, similar samples after CERN etch, had 0.3 particles per cm$^2$. "Non-embedding" garnet left $4{\times}10^4$ particles per cm$^2$ with particle sizes 1 to 5 micron. Larger particles probably were removed with RBS/Neutraclean solutions. Abrasive inclusions will create micro-areas in the lead-tin film with poor thermal contact with the copper substrate. They are likely to also be sites of electron emission at high electric field [6].

### 4.2 Magnetic field enhancement due to surface roughness

The field-enhancement model assumes that the magnetic field locally exceeds the RF critical field due to field enhancement on the boundaries between grains at different inclination. For BCP treated Nb 1.5 GHz cavities, with surface roughness of 5-10 micron, a maximum enhancement factor of 2.5 and an average of 1.5 were estimated [7]. In our SLRs there are unpolished surfaces in the electron beam weld in the high current area joining the arms to the stub. Assuming an enhancement factor of 2.5 yields a peak magnetic field of 1000 Oe at 3.8 MV/m, still under the limit of 1200 Oe but not substantially under.

### 4.3 RF Joints

Lead wire 1.6 mm in diameter was used in the joints between the cylindrical section of the SLR and the side plates. The wire was cleaned in lead stripper solution followed by a DIW rinse and dried with nitrogen just before installation. The joint in the gasket was placed in minimum current area. In SLRs, the ratio $B_{peak}/B_{maxgask}$= 9.5 which corresponds to $B_{maxgask}$=40 G at 3.5 MV/m. This maximum B field is only twice as large as the average value reported in the end-wall joint for bulk Nb interdigital resonators [8]. Nevertheless, thermometry demonstrate that, in the absence of field emission, only about 5% of the losses occur on the resonator housing [9].

### 4.4 Field emission

Intense X-ray emission above 3.6 MV/m suggests that the main factor limiting performance of ANU re-plated SLRs remains field emission, FE. The resonators were first processed with two hours of 200 Watt pulse conditioning and a few hours of multipacktoring conditioning. Pulse conditioning was done using 15 ms RF pulses at 5 % duty factor. Then Q was measured as a function of $E_{acc}$, Figure 6. In re-plated SLRs, when $E_{pk}$ exceeds 20 MV/m, Q starts to fall steeply, $E_{pk}$ =19-20 MV/m at 6 Watts. An X-ray sensor, installed two meters along the beam axis from the cryostat, displayed up to 50 μSv/hr. Both He conditioning and 200 Watt pulse power

conditioning did not improve performance substantially. Difficulties in processing FE in SLRs is caused by post-plating surface conditions: inclusions, sharp lead grain boundaries and dust particles collected during assembly in class >1000 "clean room" conditions. Unfortunately with lead plating, the use of HPR at final stage is not possible. Clean-room assembly and, in particularly, HPR eliminated FE in Nb FE-free cavities in CERN and KEK.

## 5 CONCLUSIONS

Studies of the stains on lead/tin plated SLRs improved the understanding of the films. Cracks in electron beam welds were successfully repaired with solder. Minimizing staining due to oxide films by accelerating the drying process resulted in the satisfactory performance of the SLRs. Thus this technology can lead to successful fabrication of high performance LINAC resonators at low cost - crucial for university-based laboratories.

## 6 ACKNOWLEDGEMENTS

We are grateful to a J. Noe, R. Pillay and G. Bisoffi for fruitful discussions and technicians from Nuclear Physics Department J. Heighway, A. Rawlinson, A. Cooper and H. Wallace for their important contribution in all phases of project. We acknowledge a valuable contribution in pioneering of MSA lead plating process by John W. Noe.

## 7 REFERENCES

[1] Lipski A., Noe J. and Realmuto C., "An Environment-Friendly Method for Resonator Surface Fabrication", in Proceedings of the SNEAP XXX, (K. F. von Reden and R. J. Schneider ed., World Scientific), 1996, pp.76-87.

[2] N.Lobanov and D.Weisser, "Lead Plating: ANU SLRs Upgrade", in Proceedings of the 9th Workshop on RF Superconductivity, (A.Robinson and B.Rusnak), 1999, Santa Fe, pp. 129-142.

[3] M.F.Toney, T.C.Huang, S.Brennan and Z.Rek, Journal of Materials Research, 3(2) 1988 351-356

[4] F. Palmer, in Proceedings of the 3th Workshop on RF Superconductivity, (K. W. Shepard), 1988, ANL, p. 309

[5] John W. Noe, Rev.Sci.Instrum.57(5), 1986, pp.757-760.

[6] Padamsee H., Knobloch J., Hays T., "RF Superconductivity for Accelerators", New York, 1998.

[7] Knobloch et al, "High-Field Q Slope in SC Due to Magnetic Field Enhancement at Grain Bounduries", in Proceedings of the 9th Workshop on RF Superconductivity, (A.Robinson and B.Rusnak), 1999, Santa Fe, pp. 77-91.

[8] L.M. Bollinger et.al, Nuclear Instruments and Methods in Physics Research, A553 (1993) 859-862.

[9] J.W.Noe et. al., in Proceedings of the 6th Workshop on RF Superconductivity, (ed., R.Sundelin), 1993, pp. 1052-1064.