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Electrodeposition and characterisation of lead tin superconducting films for application in heavy ion booster

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ABSTRACT

The ANU has developed experimental systems and procedures for lead–tin (PbSn) film deposition and characterisation. The 12 split loop resonators have been electroplated with 96%Pb4%Sn film to the final thickness of 1.5 micron using methanesulfonic acid (MSA) chemistry. As a result, an average acceleration field of 3.6 MV/m off-line at 6 W rf power was achieved at extremely low technological cost. Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Heavy Ion Elastic Detection Analyses (HIERDA), Rutherford Backscattering Spectroscopy (RBS), Secondary Ion Mass Spectroscopy (SIMS) and Electron Backscattering Diffraction (EBSD) revealed correlation between the substrate and film structure, morphology and the rf performance of the cavity. The PbSn plating, exercised on the existing split loop resonators (SLR), has been extended to the two stub quarter wave resonator (QWR) as a straightforward step to quickly explore the superconducting performance of the new geometry. The oxygen free copper (OHFC) substrate for two stub QWR was prepared by reverse pulse electropolishing. The ultimate superconducting properties and long-term stability of the coatings have been assessed by operation of the ANU superconducting linac over the last few years.

1. Introduction

Superconducting linacs providing precision beams of heavy ions, are one of the most successful application of rf superconductivity [1] spanning applications from small University laboratories to multibillion dollars multinational facilities. The first stage of ANU linac comprises 12 OHFC split loop resonators (SLR) electroplated with lead tin film. Multistub quarter wave resonators (QWR) with three and four gaps [2–4] have been recently developed at ANU for future linac expansion to cater for higher energies and masses.

Lead plating has been recognised as an appropriate technique at low frequency where BCS losses are low and residual losses are largely dominated by surface imperfections and trapped magnetic flux. Lead plating is preferred for substrates of complex geometry like SLRs due to difficulties in sputter coating such shapes with Nb. As superconductor PbSn alloys are superior to pure Pb due to a simpler electroplating procedure, elimination of eletropolishing step, better throwing power of the solution and lower surface resistance of the thin film. This technology provides fast moderate results with modest equipment at relatively low cost.

The copper substrate used to fabricate the resonators has a very high thermal conductivity and provides thermal stabilisation of the superconducting film even in the presence of normal conducting areas. At present besides ANU, the current lead–copper superconducting rf facilities in operation or under development are at TIFR Bombay and CIAE at Beijing. MSA chemistry (Lea Ronal Solderon MHS L) and a simple open air procedure [5] was adopted at ANU to coat the first three SLRs in November 1998. The ANU motivation was stimulated after Stony Brook abandoned fluoborate chemistry completely in favour of an "environment friendly" MSA based commercial system [6]. Although the Solderon plating solution had a nominal shelf life of one year, it was employed at ANU for three and half years without noticeable degradation of its plating capability. After that, rapid aging turned the solution yellow, Sn oxide precipitated and the throwing power decreased. In July 2002, the old Solderon solution was replaced with a similar MSA product commercially available from Schloetter, Germany. Schloetter MSA solutions supplied by the local electronics industry used to re-plate remaining nine SLRs [7,8] and electroplate the first twin QWR cavity.

The rf properties of superconducting Pb and PbSn films in accelerating structures have been reviewed in [9]. The radio frequency f dependence of the pure lead BCS resistance R_{BCS} at 4.2 K can be represented by exponent 1.75 $R_{BCS} \sim f^{1.75}$. The decreasing electron mean free path caused by the Sn fraction results in higher exponent of 1.9 compared to 1.75 for pure lead [10]. Value for the energy gap at 0 K ranges from $1.95/k_BT_c$ to $2.05/k_BT_c$ where k_B is the Boltzman constant and the critical temperature $T_c = 7.5$ K for 96%Pb4%Sn alloy. Lattice impurities decrease the mean free path causing the coherence length to decrease. As the mean free path is reduced by adding impurities,

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the BCS resistance first decreases to minimum when the mean free path is approximately equal to the pure material coherence length, $\xi_0 = 111$ nm for Pb, and then increases. For example, a PbSn alloy with Sn content of 2 to 4 at% has been found to both reduce the BCS resistance and to significantly reduce the surface oxidation rate. The surface resistance measured at 137 MHz is 2.3×10^{-8} Ω at 4.2 K and 6×10^{-9} Ω at 0 K [9].

This paper has been organised into three main sections. The first section outlines the general concept of substrate preparation and introduces the experimental procedure for the optimal PbSn electroplating. The substrate and PbSn film characterisation techniques are reviewed.

The second section presents key experimental results based on characterisation techniques including SEM, AFM, HIERDA, RBS, SIMS and EBSD used to gain information about the properties of OHFC substrate and PbSn superconducting film. The data have been systematically collected during R&D work on the ANU's linac over the last few years.

The third section presents interpretation of sample test results and relating it to the off and online performance of the linac resonators. Some possible sources limiting the ultimate resonators performance are discussed.

2. Materials and methods

2.1. Copper reverse pulse electropolishing

The surface preparation of the SLRs presents a major mechanical problem due to existence of very thin cosmetic electron beam welds used during manufacturing. Therefore the adopted surface finishing is based on combination of mechanical and mild chemical processes as described in [5]. Electropolishing (EP) has been developed for surface treatment of multi stub QWR's components as described below.

Substrates are initially mechanically polished to provide a leveled flat surface for consequent processing. The surface damage introduced by mechanical polishing has to be removed to provide fine epitaxial substrate. Therefore it is followed by EP in order to take out any subsurface damage, embedded particles or contamination. Sulfamic acid is used just before EP as a cleaning and descaling agent followed by rinse in deionised (DI) water.

In Reverse Pulse Electro-polishing (RPEP), the cathode film is kept rich in metal ions and low in impurities. During the anode polishing period, when the current is forward, the metal ions next to the cathode are depleted and a layer rich in water molecules is left. During the portion of the cycle, when the current is reversed, the metal ions from the bulk of the plating solution diffuse into the layer next to the cathode. As well during the reverse part of the cycle, gas bubbles and impurities, generated on the anode have a chance to desorb. Then the process is repeated again. Forward time is set to $t_F \sim 10$ s and reverse time is $t_R \sim 2$ s. Although it is desirable for some applications for a higher current density in the reverse (de-polishing) stage than in the forward (polishing) stage, the available power supply could only provide equal currents. The optimum current density is kept at 15 mA/cm^2 applied for three minutes. During entire process dry gas nitrogen is injected on the bottom of chemical bath in order to agitate the solution promoting the removal of H_2 bubbles generated at the anode. The electro-polishing solution is 55% H_3PO_4 mixed with 45% n-butanol. The substrate is quickly rinsed post EP and placed back into sulfamic acid following by rinse in DI water and then dried with filtered N_2. The OHFC substrate is then immediately electroplated.

2.2. Lead tin electroplating

Different combinations of plating procedures have been thoroughly investigated using the Schloetter MSA lead–tin plating bath. The throwing power of a plating solution is a measure of the ability of that solution to plate to a uniform thickness over a cathode of irregular shape such as SLR or multi stub QWR. It is influenced by the various plating parameters mainly by plating rate. Evaluation of MSA plating bath with Hull cell has revealed high uniformity at low current density but the throwing power diminishes with increasing the plating rate above 10 mA/cm^2. Based on this data, the crucial steps to achieve reliable outcomes are:

- Lead tin film is deposited at 2.5 mA/cm^2 for a film thickness of 1.0 μm.
- Mechanical polishing of existing or freshly deposited lead with wipes and alcohol instead of stripping the lead.
- Rinse thoroughly with DI high pressure water.
- 15 s soaking in plating solution.
- De-plating at 1.5 mA/cm^2 for 30 s.
- Immediately reverse pulse plating at 2.5 mA/cm^2 for 7 min for film thickness of 0.8 μm. Forward time is $t_F = 5$ s and reverse time is $t_R = 0.5$ s.
- Immersion rinse twice in DI water, the second bath containing ~0.015% ammonia. Nitrogen is bubbled through both rinse baths for a few hours in advance to reduce concentration of dissolved oxygen.

The 12 split loop resonators have been electroplated with 96%Pb4%Sn film to the final thickness of 1.5 micron achieving average offline acceleration field of 3.6 MV/m at 6 W dissipated power. The same technique, but with different setup, was used to electroplate twin QWR. Fig. 1 depicts components and assembled twin stub resonator after RPEP (a), electro-plating (b, c) and electroplated SLR (d).

2.3. Superconducting film characterisation

Numerous samples of electroplated PbSn film of different thicknesses onto copper 5×5 mm^2 substrate were prepared. The film thickness was determined by weighing small samples or by various standard analytical techniques as described below. Overall surface quality was also judged by close visual inspection. The best surfaces had light grey or silver colour.

Atomic Force Microscopy (AFM) is used for imaging and measuring the surface morphology and roughness of the sample with *X, Y* resolution up to 10 nm in ambient environment at all stages of substrate preparation process and film deposition. Vertical *Z* resolution is about 0.1 nm. Tapping mode is the choice for application with softer surface like Pb. Scans are taken at 5×5 μm^2 to estimate the roughness on length scale consistent with thin film epitaxy and superconducting rf performance.

Heavy ion elastic recoil detection analyses (HIERDA) at Nuclear Physics Department ANU has been utilised to obtain elemental concentration depth profiles in PbSn film. The technique helps to determine the elemental composition of the film and provides information about the depth profile of the sample. The typical detection limit is 0.1 atomic %, depth resolution 5 nm and lateral resolution is 20 μm. A projectile beam of ^{197}Au at $E_p = 200$ MeV is employed. Typical beam currents are 50 particle pA. The samples to analyse were positioned in a vacuum chamber evacuated with turbo pump at 10^{-7} Torr. A position-sensitive HIERDA gas ionisation detector has been used at the 14UD accelerator. Propane gas is passed through the detector at a constant pressure up to 130 mBar. The variety of samples have been analysed to explore the properties of electroplated films. The HIERDA detection operating with Au projectile beam has high and uniform sensitivity to light elements in a sample. Therefore HIERDA is complimentary to RBS allowing the detection of light elements in heavy element matrices, which is difficult with RBS.

A 1.7 MV tandem ion accelerator at the Department of Electronic Materials and Engineering (EME) ANU has been used to conduct RBS