

ENHANCED CONTROL OF ELECTROPOLISHING FOR THE PREPARATION OF THIN FOILS FOR TRANSMISSION ELECTRON MICROSCOPY: ARTIFICIAL AND MULTIPLE PHASE MICRO-ELECTROPOLISHING

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By rapidly changing voltage and current settings during electropolishing conditions can be set up for polishing otherwise difficult to polish multi-phase material. In addition a wider a more flexible range of polishing conditions can be obtained by manipulating the film build-up condition in micro-electropolishing that is normally outside the useful range of electropolishing.

Electropolishing may be broken down into two distinct processes: Macro-electropolishing or "smoothing" whereby large scale asperities are removed and Micro-electropolishing or "brightening" in which smaller ($< 1 \mu\text{m}$) irregularities are removed.¹ In "bath" (immersion) electropolishing both processes take place whereas in "jet" electropolishing the polishing mechanism is primarily micro-electropolishing. For micro-polishing to occur a thin solid film must be produced at the specimen surface.^{2,3,4,5} In order for micro-electropolishing (sometimes called brightening or brilliance) there must be random removal of metal from the surface irrespective of features such as grain-boundaries, grain orientation and defects. A number of different theories have been applied to the exact process by which the film is formed and maintained and its composition^{5,6,7,8} but again in simplistic terms as soon as the solid (typically) oxide layer is formed the removal rate is determined by the interaction between the solid film and the liquid layers rather than at the metal surface.

The optimum polishing conditions normally occur over a very restricted range of temperature, voltage and current density where film growth is balanced by film removal. Electropolishing rates and ideal polishing conditions are different for most metals and alloys,^{10,11} and in composites and multi-phase materials the technique used is normally a difficult compromise. The tight balance of conditions often means that great care must be taken in creating stable and controlled electropolishing conditions. In multi-phase/component situations it can be very difficult and sometimes impossible to find a single polishing condition in which all phases are polished acceptably and at a similar rate. One alternative is to manually change the polishing conditions (i.e. current/voltage) during the polishing process to reflect the different optimum settings for the different phases and balance polishing rates with time spent under each condition. The disadvantages of this technique are that only one phase is optimally polished at any given time resulting in inferior polishing of the other phases, and, if the total polishing time is not known in advance (as is typically the case in TEM sample preparation) the ideal times for each polishing regime will not be known. In addition the solid film itself provides a problem in multi-phase material especially when the phases have very different oxidation rates¹², where the sub-film layer becomes enriched in the slower oxidizing element (e.g. Ag in Al-Ag^{13,14} alloys and Cu in Al-Cu^{15,16} alloys).

In order to provide more routine sample preparation for superconducting composites we have developed a new method of controlling micro-electropolishing.¹⁷ We can set up "artificial" micro-electropolishing conditions that would normally be outside the "ideal" micro-electropolishing range (where film dissolution is balanced by film creation) by rapidly oscillating (≤ 1 sec/level) between low current regimes where there is

film build up and high current regimes where there is film removal. The periodic removal of the film by using the high current density level limits the level of sub-film species build up. The maximum film thickness can be controlled by both the current/voltage settings and times spent at each level. For our multiple-phase samples the applied voltage across the electrochemical cell is rapidly changed (≤ 0.1 sec/level) using square wave steps between different current densities appropriate to different phases. Different material polishing rates can then be balanced by adjusting the time interval at each setting. The rapid cycling allows for balanced polishing rates irrespective of total time.

For typical electropolishing of Nb-Ti and Nb₃Sn superconductor composites with Cu matrices we use an electrolytic solution was 2 vol.% HF_{aq}, 5 vol.% H₂SO_{4aq} and 93 vol.% methanol at a temperature of ~ -40 °C. We have found that extremely good specimens can be obtained by oscillating between 3-8 mA/mm² and 30-32 mA/mm², even for transverse cross-sections of strand less than 0.1 mm in diameter. For these specimens the oxide film can be controlled so that further surface cleaning (normally performed by ion beam thinning) is unnecessary. Balancing the polishing rates of Cu and the superconducting phase is performed by adjusting the duration at each current level, lowering the lower current level and increasing the time at that level increased the polishing rate for the superconductor and increasing the upper voltage level and increasing the time at that level increased the polishing rate for the Cu. Time intervals of 10 ms for the upper current level and 20-100 ms for the lower current have provided the best results so far.

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18. This work was supported by the US Department of Energy under Contract DE-FG02-91ER40643. The prototype electropolishing controller was constructed by Alexander A. Squitieri.