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Revealing the microstructure of Nb_3Ge superconducting films by transmission electron microscopy

A. T. SANTHANAM, P. M. YUZAWICH
Power Generation Materials Research, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, USA

The development of type II superconductors with high current carrying capacities requires close control of microstructure. This report describes a technique to prepare thin foils from superconducting films for transmission electron microscopy. Application of the technique to chemical vapour deposited Nb_3Ge superconducting films is illustrated.

1. Introduction

The successful synthesis of the A-15 compound, Nb_3Ge by a low energy sputtering technique [1, 2] and later by chemical vapour deposition (CVD) [3, 4] was an important advancement in superconductor technology. It has been shown that this material has the highest known critical temperature (~23 K) and one of the highest critical fields (380 kG near 0 K) [5]. Utilization of Nb_3Ge in superconducting magnets and rotating electrical machinery, however, depends partly on the demonstration of their ability to carry high currents. Improvement in current densities, J_c, requires close control of microstructure since the latter is believed to control the amount of flux-pinning and the current carrying capacity of type II superconductors. The microstructure of the sputtered and CVD Nb_3Ge films is on such a fine scale that it requires transmission electron microscopy (TEM) for examination. This report presents the techniques developed for preparing thin foils from Nb–Ge superconducting films for TEM. Applications of the technique to chemical vapour deposited (CVD) Nb_3Ge film are illustrated.

2. Development of technique

The details of the CVD process for the synthesis of Nb_3Ge superconducting films have been discussed by Roland and Braginski [6]. The films were typically ~12 μm thick and were deposited on Hastelloy substrates as shown in Fig. 1. The composite comprising the Nb_3Ge film and the Hastelloy substrate will hitherto be referred to as "Nb_3Ge tapes".

The sequence of steps involved in the preparation of thin foils from the Nb_3Ge tapes is illustrated in Fig. 2. The thickness of the substrate (~50 μm) is just sufficient to provide mechanical support to the brittle Nb_3Ge film during handling and subsequent thinning. Discs, 3 mm in diameter, are punched from the tape and thin foils are prepared from the 3 mm discs in a two step process as described below.

(a) Removal of substrate from the central portion of the 3 mm disc.

(b) Thinning of the exposed Nb_3Ge film.

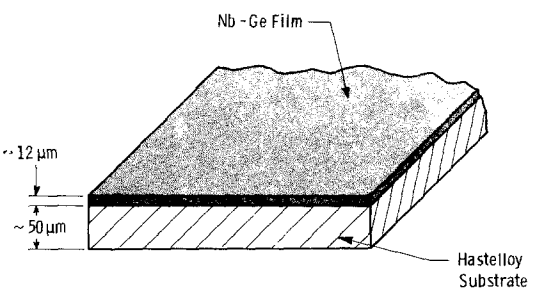

Figure 1 Schematic drawing of the Nb–Ge film chemical vapour deposited on Hastelloy substrate.

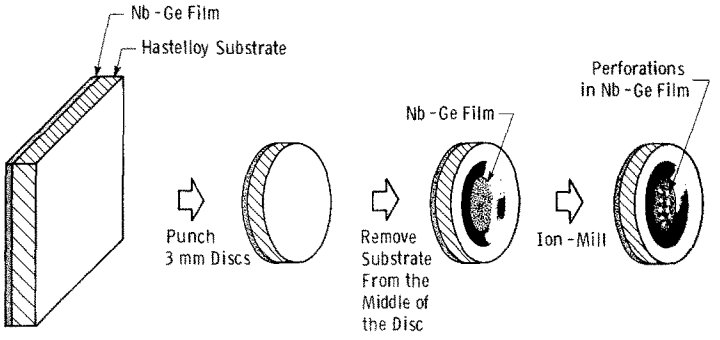

Figure 2 Sequence of steps involved in the preparation of thin foils from Nb–Ge tapes for TEM.

2.1. Removal of substrate from the Nb_3Ge tape

The 3 mm disc punched from the Nb_3Ge tape is placed in an electropolishing specimen holder such that the central portion of the Hastelloy side of the disc is exposed to the electrolytic solution. The Nb–Ge side of the disc is covered with a piece of 0.003 in. thick teflon sheet which serves the dual purpose of protecting the Nb_3Ge film from possible electrolytic attack as well as providing a cushion for the brittle Nb_3Ge film. The specimen holder with the disc in position is mounted on a jet electropolishing unit (Fig. 3) which is subsequently placed in a clear glass beaker to enable specimen observation during electropolishing. The electrolyte consists of 100 ml sulphuric acid and 600 ml methanol. Electropolishing is carried out at 20° C using a platinum coil cathode and a current of 35 mA. The jet is set at moderate speed in the beginning and is directed at the exposed Hastelloy. When the Nb–Ge film begins to appear, the jet flow is decreased to avoid the Nb–Ge film rupture. The Hastelloy substrate is removed in about 2 min and the Nb_3Ge film in the middle of the disc is exposed to the solution. The electrolyte attacks the Nb_3Ge film at a much lower rate than it attacks the Hastelloy substrate. The slight electrolytic attack on the Nb_3Ge film actually helps in the removal of any diffusion layer that may be present near the substrate.

2.2. Thinning of the exposed Nb_3Ge film

The sample is carefully removed from the holder and washed in methanol. Attempts to thin the Nb_3Ge film electrolytically using sulphuric acid–hydrofluoric acid solutions in various concentrations did not yield satisfactory foils. Chunks of material were often removed leaving holes with no thin areas for electron transmission. On the other hand, thin foils were successfully obtained by ion bombardment in Commonwealth Scientific Corporation's Ion MicroMilling

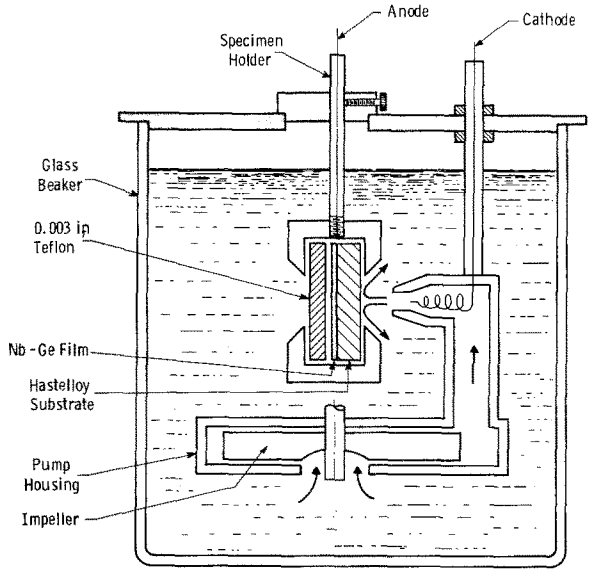

Figure 3 Hastelloy substrate removal in jet electropolishing apparatus.

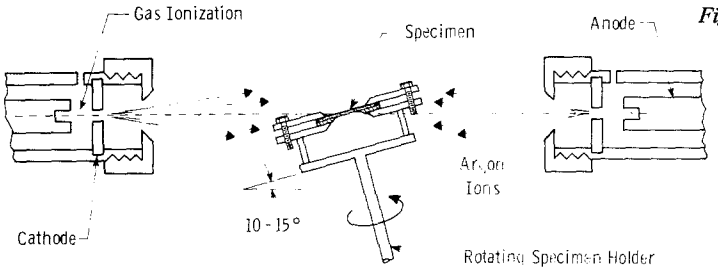

Figure 4 Schematic illustration of ion milling.

Instrument (IMMI)-Model III as described below.

The 3 mm disc, with the substrate removed from the centre, is mounted in the specimen holder of the instrument and is placed in the milling chamber shown schematically in Fig. 4. The chamber is evacuated to less than 1×10^{-5} Torr and argon is admitted to each ion gun. The argon flow is controlled to maintain a chamber pressure of 5×10^{-4} Torr. A potential of 7 kV is applied between the anode and cathode plate. The latter has a hole in the centre which allows a stream of ions to bombard the specimen from both sides as illustrated in Fig. 4. The specimen is set at an angle of 10 to 15° to the ion beam and is rotated to obtain uniformly thin areas. A milling rate of $\sim 2\,\mu m\,h^{-1}$ was obtained with an ion current of $\sim 100\,\mu A$. The specimen can be observed during ion milling by means of a low power microscope attached to the milling chamber. The ion bombardment is stopped when several perforations appear in the Nb_3Ge film. At this point the foil is very clean with sufficient thin areas between perforations. The foil is, however, extremely fragile and care should be taken in its removal from the specimen holder.

3. Structure of the Nb_3Ge film

The CVD Nb_3Ge foil was examined in a Philips EM-300 transmission electron microscope operating at 100 kV. A typical micrograph is shown in Fig. 5. Roland and Braginski [6] reported that the CVD Nb_3Ge tapes exhibit a [1 0 0] columnar texture. The structure presented in Fig. 5, therefore, represents a section normal to the columnar growth direction. The mean diameter of these columnar grains as measured from the micrograph by the linear intercept method is ~2500 Å. It is interesting to note that the grain boundaries are often curved in contrast to the equiaxed grains observed in other A-15 compounds such as V_3Ga [7], Nb_3Sn [8] that are produced by diffusion reaction. In addition to grain boundaries, one can observe stacking faults in the structure. Precipitates ~300 Å in size can also be seen in the structure, but their number density is low. The significance of these microstructural features with regard to flux pinning is being explored.

4. Other applications

The technique described here can be applied to other metallic or ceramic systems where the film is formed on metallic or ceramic substrates. For example, the physical vapour deposited (PVD) coatings on superalloys and refractory metals can be examined in TEM using the above technique. While metallic substrates can be removed electrolytically, ceramic substrates generally require ion-milling.

Several precautions must be taken in the application of this technique. Thicker substrates need some grinding. In such cases the film must be protected by lacquer during grinding. In the case of metallic substrates, suitable electrolytes should be chosen so that the film is not attacked. To prevent film rupture and to obtain large thin areas the angle of incidence for the ion beam

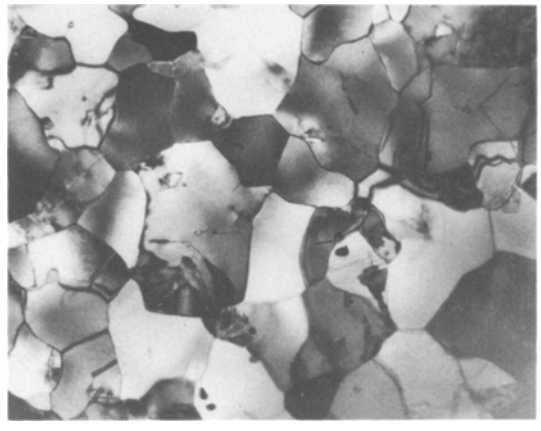

Figure 5 Transmission electron micrograph of CVD Nb_3Ge superconducting film, X 40 000.

should be decreased in the final stages of ion milling. It would be advisable to choose proper ion milling parameters (accelerating voltage, ion current, gun current, etc.) for each system so that no perceptible ion damage is introduced into the specimen.

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