THE ANGULAR DEPENDENCE OF Nb_3Sn CRITICAL CURRENTS IN TRANSVERSE MAGNETIC FIELDS

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The dependence of critical currents of vapour-deposited and diffusion-processed Nb_3Sn tapes on the magnitude and direction of magnetic field perpendicular to the current is experimentally investigated. By comparing the experimental results with theoretical considerations we conclude that the form of grains in the vapour-deposited samples is almost sinusoidal, whereas for the diffusion-processed ones it is more ellipsoidal. For both kinds of tapes, detailed structural microanalysis (electron microscopy, scanning electron microscopy, optical microscopy) of the substrate and the Nb_3Sn tapes has been performed in order to explain the existence and the character of the above mentioned dependences from the processes of the grain formation.

1. INTRODUCTION

One of the most important features of inhomogeneous type II superconductors is their ability to carry large transport currents up to the upper critical field H_{c2}. Both theoretical and experimental investigations have attributed this capability to the pinning of the fluxoid lattice by heterogeneities and various defects (dislocations, precipitates, grain boundaries, surfaces, point and other defects).

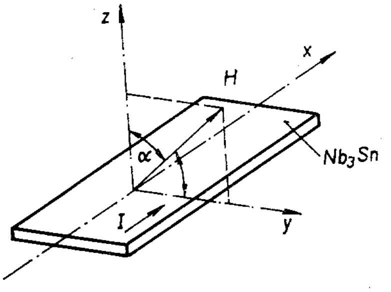

Fig. 1. Nb_3Sn superconducting tape in transverse magnetic field.

The surface pinning in a superconductor determines its critical current in the case of a very homogeneous conductor (where the volume pinning is almost negligible). The character of the grain-boundary pinning is very similar to the character of the surface pinning. Therefore, in current materials where the density of such boundaries is quite large, the pinning on the grain boundaries may be the determining factor of current-carrying capacity, as it is generally supposed to be the case in Nb_3Sn.

Let $I_{c\parallel}$ and $I_{c\perp}$ be the critical currents of the tape in the external magnetic field ($H \perp I$) parallel ($\alpha = 90°$) or perpendicular ($\alpha = 0°$) to the tape (Fig. 1). The angular dependence of the critical currents of the tape in transverse magnetic field will be then characterized by the ratio $I_{c\alpha}/I_{c\perp}$ where α is generally in the region 0° to 90°. The ratio $I_{c\parallel}/I_{c\perp}$ will be called in the following text the anisotropy of the critical current.

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Both the angular dependence and the anisotropy of critical currents of Nb_3Sn tapes in transverse and longitudinal magnetic fields have already been studied experimentally by several authors. The anisotropy of diffusion processed tapes was investigated rather extensively by MONTGOMERY [1], BENZ [2, 3], JERGEL and HLÁSNIK [4] and CASLAW [5]. The results of Refs. [1, 4] show $I_{c\parallel}/I_{c\perp} > 1$ whereas BENZ and CASLAW did not find any angular dependence of I_c at all. The anisotropy of vapour-deposited tapes in transverse magnetic field has been described by MONTGOMERY [1] and SCHINDLER and NYMAN [6]. It is interesting to note that for this kind of tape $I_{c\parallel}/I_{c\perp} < 1$, being a constant (about 0·65) in the region of magnetic fields from 100 to 180 kOe. The angular dependence of critical currents on the longitudinal component of magnetic field has been experimentally studied by CODY et al. [7, 8]. DETTMANN and LANGE [9] performed the investigation of anisotropy of Nb_3Sn on samples formed by electrochemical plating of Sn onto Nb substrate with following heat treatment. In this paper we shall deal with Nb_3Sn tapes prepared by vapour deposition and diffusion processes only.

In the papers mentioned above [1–6] the reason of the angular dependence of critical currents in transverse magnetic fields is explained rather insufficiently. BENZ [2, 3] suggested that for his diffusion processed tapes the lack of anisotropy was due to the very fine Nb–Sn structure associated with the process. CASLAW [5] attributes the homogeneous nature of the flux pinning centres in superconducting layer for different orientations of the transverse magnetic field vector to the third material – copper, which changes the reaction kinetics of the niobium–tin system. Theoretical evaluation of the angular dependence of pinning and its connection with different and possible grain shapes is derived for Nb_3Sn tapes in [10]. The main purpose of the following paper is therefore to complete the previous experimental study [4] of the angular dependence and anisotropy of critical currents for both vapour deposited and diffusion processed Nb_3Sn tapes. Then by analysing the microstructure of the materials mentioned above as well as by comparing these results with the theoretical conclusions [10] we try to explain the existence and the character of dependence obtained by experiments.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of samples for electrical measurements

2.1.1. Vapour deposited tapes

The measurements were performed on short samples, 12 cm in length.

The vapour-deposited samples were prepared by the simultaneous hydrogen reduction of niobium tetrachloride and tin dichloride vapours [11] on AKVN-type stainless steel substrate 50 μm thick and 3 mm wide [12]. The thickness of the Nb_3Sn layer was about 7·5 μm.

2.1.2. Diffusion-processed tapes

The basic procedure for the preparation of diffusion-processed samples is quite simple, and is described in more detail elsewhere [13–15]. Here we give only a brief outline. A thin niobium substrate about 15 μm thick was coated with tin and then heat-treated at 1000 °C in a vacuum of 10^{-5} torr for 20 minutes. Neither the samples nor the materials of the samples were subjected to any other treatment.

2.1.3. Sample testing

Identical experimental conditions have been used for electrical measurements of all samples. Each sample (3 mm wide) was placed in a groove of a brass plate. This plate acted both as a mechanical support and as a shunt, protecting the tape from excess current in the normal state. Current and voltage leads were then attached to the sample in the usual four-probe resistance measurement configuration. The measuring procedure has always been the same; the samples were cooled down to 4·2 K with the magnetic field turned off and were oriented in a configuration with field transverse to the transport current. Measurements up to 50 kOe were done in a superconducting solenoid. The orientation of the tape has been fixed by a special milled-down substrate with a well-known angle. The critical current was taken as the current at which the voltage across the sample of 0·5 μV was detected between two points, 20 mm apart.

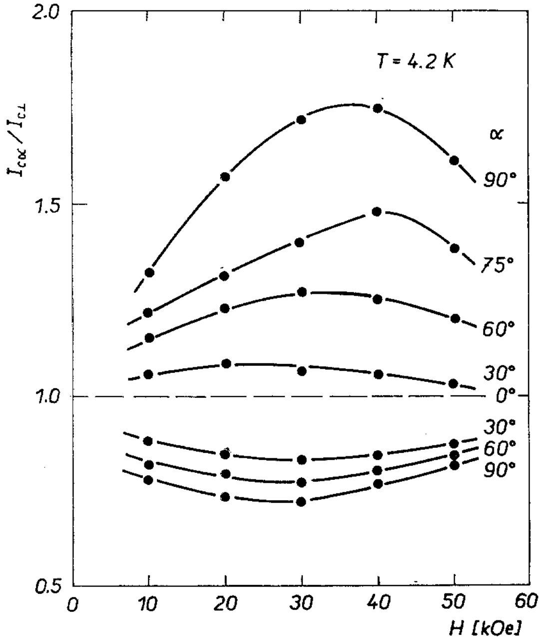

Fig. 2. The magnetic field dependence of the ratio $I_{c\alpha}/I_{c\perp}$ for various angles: a) tape prepared by diffusion process, b) tape prepared by vapour deposition.

2.1.4. Results

Typical field dependence of critical currents for various orientations of tape in transverse magnetic field is plotted in Fig. 2 at angles $\alpha = 0$, 30, 60 and 90° for vapour deposited tape and $\alpha = 0$, 30, 60, 75 and 90° for diffusion processed tape. It is interesting to note that the maximum for the diffusion processed tape varies appreciably with the angle and lies between 2 and 4 kOe (in the same region is also the minimum for the vapour deposited sample). For the time being we are not able to explain the existence of this maximum or minimum because the nature of the pinning centers in Nb_3Sn is not exactly known to date.

The idea of different field dependence of the various pinning centers seems plausible (maybe some of the pinning centers are efficient in certain magnetic field region only).

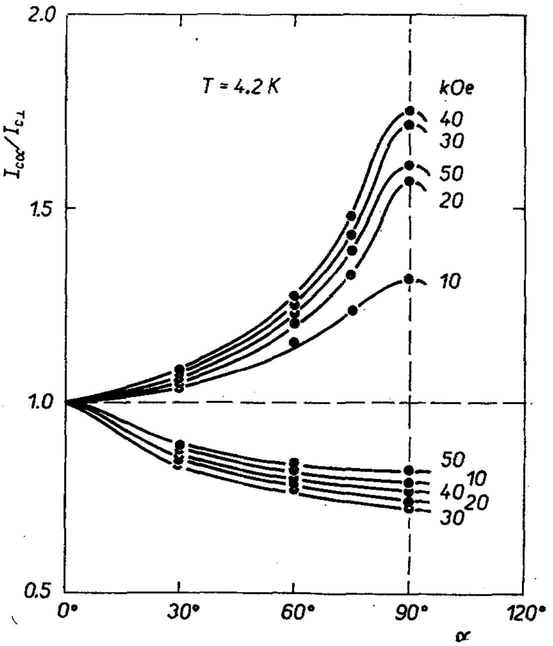

Fig. 3. The angular dependence of the ratio $I_{c\alpha}/I_{c\perp}$ for magnetic fields between 10 kOe and 50 kOe for samples of Fig. 2.

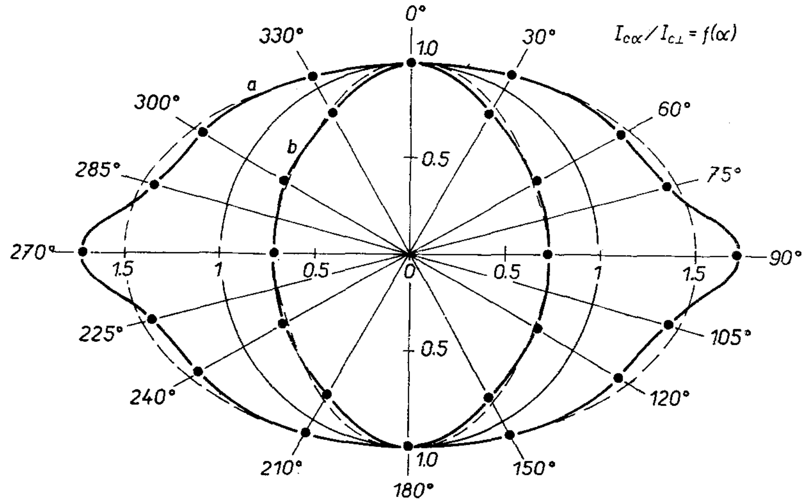

Fig. 4. The polar diagram of $I_{c\alpha}/I_{c\perp}$ for (a) diffusion processed and (b) vapour deposited tape from Fig. 2 (at 30 kOe). The measurements were carried out in the two upper quadrants. The dashed lines are the theoretical curves for ellipsoidal ($a/b = 1{\cdot}5$) and sinusoidal ($a/b = 0{\cdot}72$) grains [10].

Figure 3 shows the angular dependence of the critical currents for vapour deposited and diffusion processed tapes. One may see the difference in the shape of the angular dependence of $I_{c\alpha}/I_{c\perp}$ for the two types of tapes. The polar diagram of the angular dependence of critical currents for the previously mentioned samples is plotted in Fig. 4. The curve outside the unit circle is for the diffusion processed tape, inside the circle for the vapour deposited tape.

For the comparison with theory, the calculated angular dependence of pinning for ellipsoidal and sinusoidal shapes [10] of the Nb_3Sn grains is plotted in this figure, too.

3. STRUCTURAL MICROANALYSIS

3.1. Vapour-deposited tapes

3.1.1. Preparation of samples for electron microscopy and scanning microscopy.

The tapes coated by Nb_3Sn layer prepared by deposition process were examined indirectly by preparing celluloid replicas from the sample surfaces or directly by a scanning electron microscope, respectively. Far greater resolutions were obtained by transmission electron microscopy through thin foils made directly from deposited Nb_3Sn layers.

The two-stage celluoid replicas allowed to obtain an image about the building of deposited layer. This was mainly in the case of very thin Nb_3Sn layers when, because of the 1 to 2 μm thickness we were not able to obtain thin foils suitable for transmission electron microscopy. The replicas were taken from the surfaces by well-known method immediately after they were taken out of the deposition chamber.

The thin foils suitable for transmission electron microscopy were prepared as follows. The tape was cut into small pieces of about 2 × 3 mm and left several hours in etching solution (50% HCl + 10% HNO_3 + 5% H_3PO_4 + 35% H_2O) at room temperature to dissolve the backing. The solution dissolved the stainless steel as well as the intermediate compounds which were formed at the Nb_3Sn-stainless steel, leaving only small, brittle pieces of Nb_3Sn. The acid solution was decanted and the obtained pieces washed in distilled water and alcohol.

Individual pieces of Nb_3Sn were transferred onto a platinum mesh and chemically thinned in solution of 1 HF : 3 HNO_3 : 4 H_2O [16] or 1 HF : 3 HNO_3 : 1 H_2O [17] respectively, at room temperature in a polythene beaker. The samples were rapidly thinned, therefore it was necessary to take them out in a convenient moment and to transfer them into distilled water. After this operation they were gradually washed in alcohol, acetone, benzene, rinsed and placed between two grids. The samples were thinned either into a wedge around the sample or were pin-holed through the whole area depending upon the sample composition. Samples were then examined by JEM-7 electron microscope.

At the same time the examinations on scanning electron microscope JSM-U 3 were performed directly from the deposited sample surface to verify the authenticity of the image obtained by electron microscope replicas.

3.1.2. Results

A number of samples prepared by several deposition technologies have been examined. From the existing examinations one could say that the process of deposition onto stainless steel substrate begins epitaxially, likely on grain boundaries, which is in direct relation to the thermodynamic laws. The sample shown in Fig. 5 (Appendix I, p. 680a) is made by celluloid-replicas method from a deposited thin layer. After covering the substrate surface the deposited material starts to grow in the direction perpendicular to the surface. On the surface the deposit itself creates sharp formations, cf. Fig. 6 (Appendix I, p. 680a), which after verifying their authenticity by scanning microscopy look as in Fig. 7 (Appendix I, p. 680b). The differences in surface shape between Fig. 6 and Fig. 7 are caused by the use of different scanning techniques (the "holes" which one can see in Fig. 7 are in Fig. 6 filled unsatisfactorily and they are covered over by celluloid replica only. The image character remains the same).

The grains of Nb_3Sn themselves may be seen from transmission electron micrographs prepared from thin foils. The range of observed average grain size was 0·2 to 1·5 μm. A typical micrograph is shown in Fig. 8 (Appendix I, p. 680b). The grain size was large enough to obtain diffraction patterns from single grains using selected-area electron diffraction as it is shown in Fig. 9 (Appendix I, p. 680c). In the case of diffraction ring patterns from greater number of grains taken by electron beam the lattice spacing calculated from these rings agreed very well with already published data [17].

In conclusion one can say that the deposited Nb_3Sn material begins to grow on the substrate surface epitaxially from the nuclei. After filling up the free substrate space the Nb_3Sn begins to grow preferentially in perpendicular direction to the substrate surface, therefore one can assume that in this direction the grain size should be greater. On the top of the surface sharp edges are created.

3.2. Diffusion-processed tapes

3.2.1 Preparation of samples for optical microscopy

The already well-known methods have been used for examination of niobium substrate surface by optical microscopy. The surface of the niobium tape, prepared by powder metallurgy process, was etched by chemical solution of approximately 1 part of concentrated HF, 1 part of concentrated HNO_3, and 1 part of distilled water at room temperature (Fig. 10, Appendix I, p. 680c). Simultaneously the method of thin tinning of the substrate surface at low temperatures (600 to 700 °C) was used. At these temperatures tin clusters as well as elongated formations in the rolling direction were created (Fig. 11, Appendix I, p. 680d).

3.2.2 Results

The diffusion of tin into niobium takes place preferentially along the various defects (grain boundaries, dislocations, slipping planes, etc.). In our case it should act mainly along the grain boundaries destructed by the rolling process. Then the new Nb_3Sn phase would preferentially fill up and/or follow these deffects on the surface. After this process is over the Nb_3Sn phase will penetrate into the interior of the substrate itself. As a result one could say that the distribution and orientation of Nb_3Sn phase is determined by the niobium substrate structure, by the method of its preparation and composition [18]. It seems plausible to speculate that at temperatures at which the tinning process begins, in the niobium substrate some internal strain removing processes take place, too. Figure 12 (Appendix I, p. 680d) shows the structure of substrate tape prepared by means of electron beam melting, etched by tin.

As a conclusion from the results shown above it should be possible to assume that the grains of the Nb_3Sn should have rather plane shape with the orientation parallel to the surface.

4. DISCUSSION

It is evident from the experimental results that the diffusion-processed tapes have larger critical currents in transverse magnetic fields parallel to the surface of tapes, whereas the vapour-deposited ones in fields perpendicular to the surface. This is also true for fields higher than those used in our experiments [1]. From our theoretical considerations [10] we can deduce that in the former case the dimensions of the grains are larger in the direction parallel to the tape surfaces, in the latter case perpendicular to the surface of the tapes.

For the diffusion-processed tapes such arrangement is caused by the diffusion process itself, because of its penetration into the substrate along the Nb grains which are already flattened by the rolling process (Fig. 11).

In the process of vapour deposition the situation is quite different. Because of the rapid growth of the grains from the gaseous components the dimensions of the grains in the direction of the growth can be larger than the size of grains parallel to the substrate surface. From the transmission electron-micrographs (Fig. 5) we can see that the grains follow the structure of the substrate.

The calculated angular dependence of the pinning indicates sinusoidal shapes of the grains in the vapour deposited tapes (the changes are small near $\alpha = \pi/2$) and more ellipsoidal shapes for the diffusion-processed tapes (larger decrease near $\alpha = \pi/2$). We think that this can be understood from the process of the crystal growth, too. In vapour deposition the grains grow from the nuclei on the substrate, they can therefore have some sharper edges on the substrate surface itself. The final surface of the grains is also of such a form (Figs. 6, 7), or nearly pyramid-like.

A different situation arises for the diffusion-processed tapes. Here the diffusion of Sn takes place first along the Nb grain boundaries (Fig. 10). These grains are almost ellipsoidal, the Nb_3Sn grains will have an analogous structure. Therefore we can expect ellipsoidal Nb_3Sn grain shapes which are somewhat elongated at the edges near the larger semi-axis (because of better space filling).

The anisotropic properties of Nb_3Sn tapes could have very serious consequences in the building of superconducting devices (mainly magnets), and every manufacturer therefore should suppress as much as possible such unsuitable behaviour. The usual way of tape orientation when the electrical properties are measured is the transverse magnetic field perpendicular to the wider side of the tape. However, in the winding of the solenoid the tape is parallel with the field (at least for the central plane of the solenoid). Then for the diffusion-processed tape the dangerous place in which the solenoid may go normal is somewhere in the outside corner of the winding [4], (depending upon the design of the winding) whereas for the vapour-deposited one it is in the central part of the winding where the maximum axial component of the field is situated. One could presume that similar anisotropic behaviour as for the critical currents of vapour-deposited and diffusion-processed Nb_3Sn tapes in transverse magnetic fields will take place for the resistive state of the superconductor, too.

One very important question still remains to be answered. It is the explanation of the existence of maxima and minima in the field dependence of critical currents and the angular dependence of their position as well as the magnetic-field dependence of I_c at various angles.

We assume that the existence of grains of various dimensions can cause different magnetic field dependence of the pinning on these grains. So, e.g., it is possible that the Nb_3Sn grains formed at the beginning (Fig. 10) of the diffusion processes have larger dimensions than the grains which are formed on and/or along smaller defects in the deeper part of the tape. Therefore, the magnetic field dependence of their pinning may also be of different kind. A similar situation arises in the vapour deposition process (Figs. 5, 8), where smaller grains are created, too (maybe because of better space filling). Solution of this problem will be the subject of our further study.

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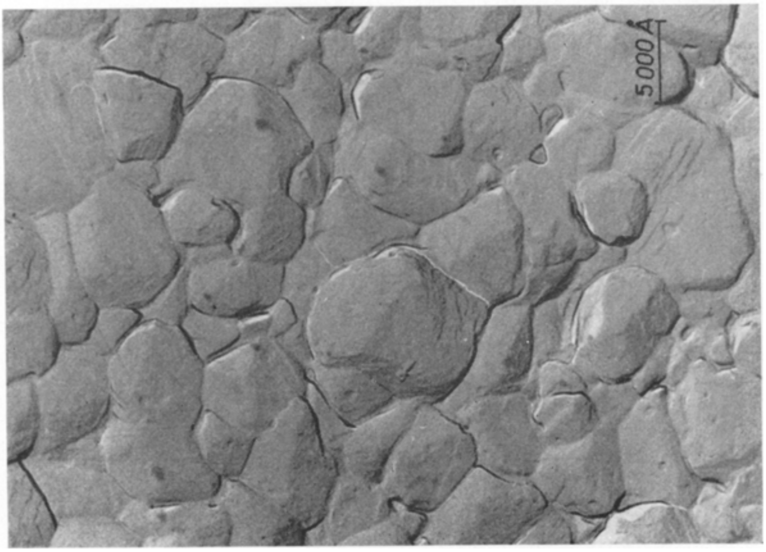

Fig. 5. Electron micrograph of deposited thin layer (celluloid replica).

Fig. 6. Electron micrograph of deposited layer about 7·5 μm thick (celluloid replica).

Appendix I: *Jergel M. et al.*: The angular dependence of Nb_3Sn critical currents ... (p. 644).

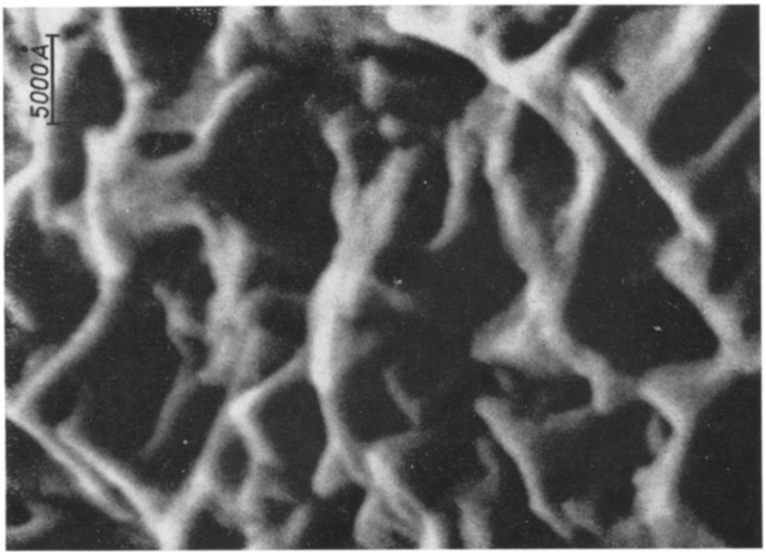

Fig. 7. Micrograph of the same surface as in Fig. 6 taken by the scanning microscope.

Fig. 8. Transmission electron micrograph of Nb_3Sn layer.

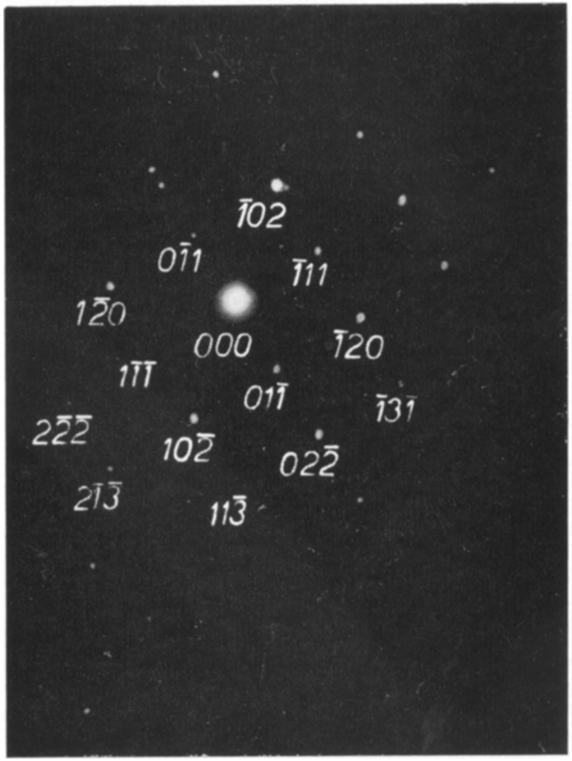

Fig. 9. Selected area electron diffraction pattern of a (211) crystal.

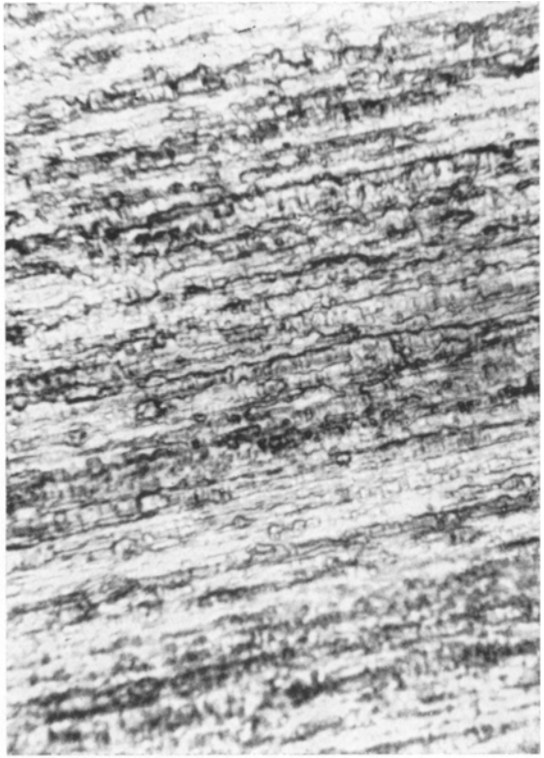

Fig. 10. The structure of the surface of niobium tape prepared by powder metallurgy. Etched (1260×).

Appendix I: *Jergel M. et al.:* The angular dependence of Nb_3Sn critical currents …
(p. 644).

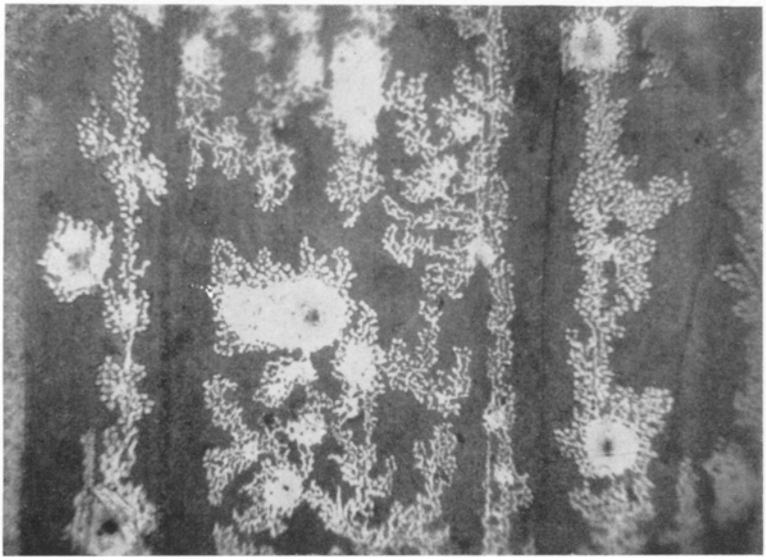

Fig. 11. The beginning of the tin diffusion into the same niobium substrate as in Fig. 10 (1260×).

Fig. 12. The structure of the surface of niobium tape prepared by electron beam melting. The tape is tinned at higher temperature (700 °C), (630×).