

THE PREPARATION OF SUPERCONDUCTING Nb_3Sn -
SURFACES FOR RF APPLICATIONS

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1. Introduction

For HF-applications, a superconducting material with high energy gap $\Delta \sim T_c$ from general considerations offers some more or less realistic advantages compared to a superconductor with a lower Δ /1/. These potential advantages are

1. a higher working temperature (for $R_{res}(Nb) \approx R_{res}(Nb_3Sn)$)
2. a better thermal stability "
3. a higher superconducting limit ($B_c \sim T_c$)
4. a lower surface resistance R_S (if $R_{res}(Nb_3Sn)$ can be reduced)

At the moment niobium - the element with the highest T_c (9.2 K) - is nearly always used in superconducting HF-applications. Any material with a higher T_c must be an alloy or compound. The highest T_c is found for A15-compounds, and in this class of material most work has been done for Nb_3Sn with a T_c of about 18 K. Therefore it is reasonable to study the HF-properties of this well-known superconductor.

On the other hand, with Nb_3Sn , also some disadvantages must be expected. These are:

1. bad thermal conductivity
2. no possibility of shaping
3. formation of unwanted phases such as Nb_6Sn_5 and $NbSn_2$
4. increase of costs.

The first two difficulties prescribe to coat cavity-shaped substrates with a thin layer several penetration lengths thick, the other ones must be overcome by a good preparation method.

Nothing can be said in advance whether a Nb_3Sn surface will give a low residual resistance or exhibit a small electron secondary emission coefficient.

2. Choice of preparation method

Most work on Nb_3Sn concerns the development and production of a superconductor with a high current density, and this means that there are inhomogeneities acting as pinning centers. Especially for Nb_3Sn grain boundaries are thought responsible for the high current densities observed. For a HF-superconductor, however, inhomogeneities are unwanted as they may trigger thermal breakdown *). For this reason the RCA-method - the transport of Nb and Sn via the gasphase - was ruled out, though it might allow the deposition of a Nb_3Sn -layer on a good thermal conductor like Cu.

*) As far as known little experimental or theoretical work has been done to study the efficiency of a given inhomogeneity to initiate a breakdown. Therefore it is not sure whether a high current density and good HF-properties are incompatible.

The most natural substrates for the Nb_3Sn -layer is a Nb-cavity. Then only one component - the tin - must be transported to the substrate. Plating the Nb with tin electrolytically or by evaporating on the cold substrate seems unfavourable as during the heating up there will form wrong phases (Nb_6Sn_5 , $T_c = 2.1$ K, and $NbSn_2$, $T_c = 2.7$ K), which may be hard to completely remove afterwards. Therefore we decided to apply a method, where the substrate is exposed to tin vapour at a high temperature, and so did other groups (KfK Karlsruhe /2/, Wuppertal /3/, MIT /4/). From the phase diagram Nb-Sn one can see that the reaction temperature should be higher than 930° , because in this case Nb_3Sn is the only existing compound.

In the literature, it is assumed that the growth of a Nb_3Sn -layer takes place by the diffusion of tin through the grain boundary to Nb substrate (e.g. /5/), though this mechanism is not really proven. If this is true we need a fine network of grain boundaries to obtain a layer of homogeneous thickness. In our first experiments we saw that there are nucleation problems for Nb_3Sn , if Nb is simply exposed to tin vapour. But we found out that the nucleation problem may be overcome by preanodising the niobium substrates and heating in a temperature gradient or adding a small amount of SnF_2 . This is documented by Fig. 1.

Furthermore it turned out that the Nb_3Sn may be contaminated with Si from the quartz tube in which in our case the reaction takes place. Therefore we introduced a reaction room with niobium walls only.

3. The standard preparation procedure

The arrangement in which we prepare our Nb_3Sn -cavities is shown in Fig. 2. Our standard procedure is characterized by the following points.

1. A continuously pumped quartz tube (turbomolecular pump).
2. A reaction room with niobium walls only. It is evacuated through the leakage between resonator and the bottom plate.
3. Preanodisation of the niobium surfaces to be covered.
4. Heating up in a temperature gradient (Sn hotter) or adding a small amount of SnF_2 . The furnace is preheated to 750°C .
5. Annealing for three to four hours at 1050°C ,
6. Cooling within the furnace (vertical axis) by blowing cold air from below with a ventilator.
7. Cleaning of the Nb_3Sn -surface by oxipolishing (anodising in NH_3 -solution and dissolution of the oxide in HF).
8. Wet installation (as with niobium cavities).

The parameters of preparation are generally not critical. For instance one may vary the annealing temperature, duration, pre-anodisation voltage, start without preheating, increase the leakage of the niobium reaction room and will not find a pronounced effect.

In what way the preanodisation works is not clear. One may simply say that we produce a disturbed niobium surface which in connection with a higher tin supply by the temperature gradient or SnF_2 enables easy nucleation.

4. Results of HF-measurements

In table 1 some of our best microwave results are represented. A critical flux density B_c^{ac} of 100 mT may be obtained. Generally B_c^{ac} seems to be temperature independent. The best quality factors (low field) were $9 \cdot 10^9$ at 1,5 K and $2.7 \cdot 10^9$ at 4.2 K. Average values are 2 to $3 \cdot 10^9$ at 1.5 K and 1 to $2 \cdot 10^9$ at 4.2 K. All measurements were made at 9.7 GHz for TE_{011} - and TM_{010} -type cavities.

We have made a great number of preparations after the standard procedure but usually with some minor modification such as the temperature and duration of annealing, the time for heating up or cooling down. Therefore we can make a statistic and represent

every preparation by its best B_c^{ac} -value at 1.5 K. In Fig. 3 the relative frequency of B_c^{ac} -values in a certain interval is plotted against B_c^{ac} of the middle of this interval. The points are experimental, the curve is a calculated Gauß distribution. The good agreement demonstrated that our results are dominated by statistical defects.

5. Analysis of Nb₃Sn-layers

By our procedure we obtain a dense layer of Nb₃Sn 1 to 2 μm thick and with a grain size also of about 1 μm (Fig. 4). If such a layer prepared on a niobium sheet is bent, intercrystallin fracture in the Nb₃Sn occurs (Fig. 5). The grain boundaries are weak links as it is to be expected by their contribution to grain growth (tin enrichment). After a thermal treatment for some hours at 1050 °C without tin source the fracture becomes transcrystalline (Fig. 6), indicating a "cleaning" of the grain boundaries. X-ray measurement revealed that the Nb₃Sn still is polycrystalline. Unfortunately this thermal treatment caused no improvement of the microwave properties neither in critical fields nor in quality factors. The results even were a little below the average.

The temperature independent B_c^{ac} and the rather rough polycrystalline surface can be taken as a hint that at some potrusion the superconducting critical field is surmounted. Then it would be good to smoothen the surface by polishing. Therefore the development of smoothness with oxipolishing was studied by SEM. Thereby we found out that after a total anodisation voltage of about 200 V pitting occurs as demonstrated in Fig. 7. The holes generally appear within the grains, but sometimes also in the boundaries. We could not prevent pitting neither by changing the electrolyte for anodisation nor by decreasing the dissolution velocity nor by chemical polishing nor by electropolishing. The reason for the pitting is not known, but the great number of pitting holes shows that it must be connected intimately with the structure of the Nb₃Sn-layer.

A number of AES-measurements revealed that under our conditions we obtain rather pure Nb₃Sn-layers. Also the contamination by C and O is small. Without oxipolishing there is a tin maximum on the surface and an oxygen maximum just below the surface coinciding with a tin minimum. Also with AES we could show that in an intermediate stage (e.g. in the temperature region of about 800 °C) there is N-rich layer in the upper part of the niobium, probably NbN, but it seems to play no decisive role, because we obtain the same Nb₃Sn structure when we start with an oxide layer grown in pure water.

6. Conclusion

The best microwave results and even the average values we reached with Nb₃Sn could suffice for an accelerator layout as at present is usual. But the broad Gaussian curve (Fig. 3) shows that statistical defects exert still too large an influence. It will be necessary to suppress this defects to get a much smaller Gauß distribution. Another point is to use Nb sheet resonators as substrates instead of the bulk niobium cavities.

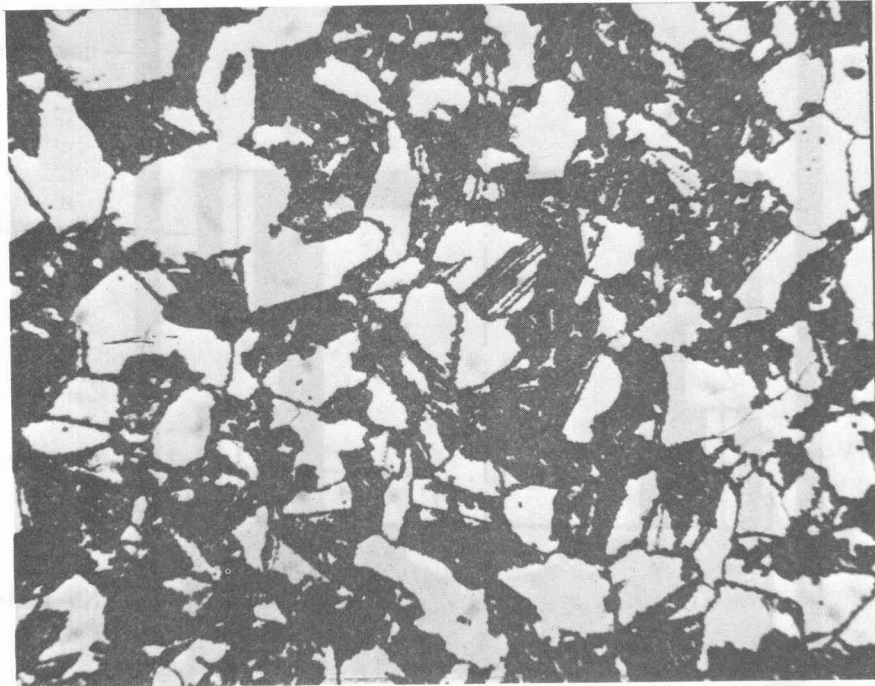
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Literature

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- /4/ V. Diadiuk e.al.: IEEE Transactions on Magnetism, MAG-15, (1979) 610.
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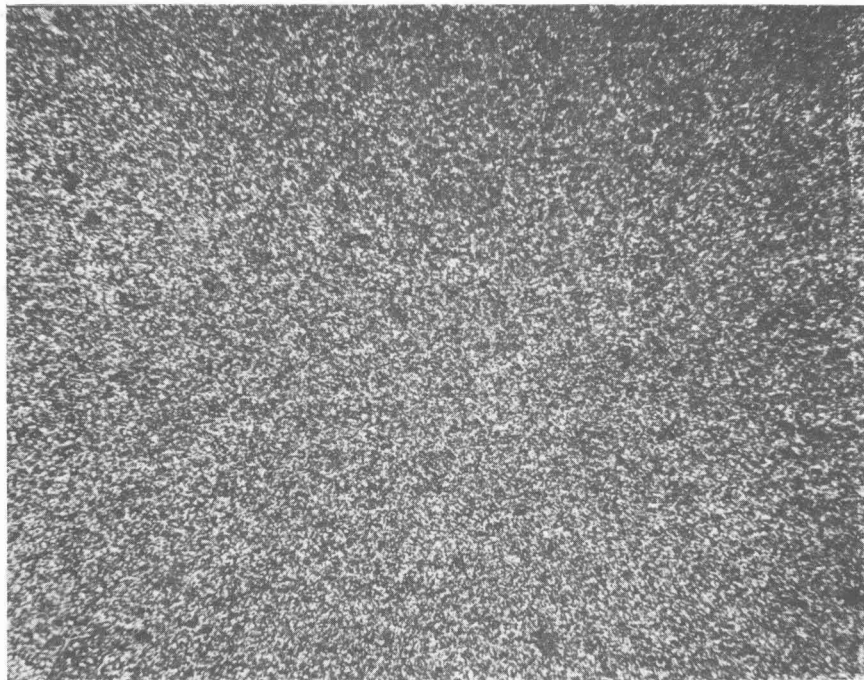
Preparation method	1.5 K			4.2 K		
	B_C^{ac} mT	$Q(B_C^{ac})$	$Q(0)$	B_C^{ac} mT	$Q(B_C^{ac})$	$Q(0)$
inner reaction room quartz HF-cleaned	100	$1.0 \cdot 10^9$	$2.4 \cdot 10^9$	-	-	$1.7 \cdot 10^9$
preanodised + temperature gradient	106	$1.0 \cdot 10^9$	$1.6 \cdot 10^9$	> 78	$4.9 \cdot 10^8$	
preanodised + temperature gradient	84	$1.8 \cdot 10^9$	$2.5 \cdot 10^9$	84	$8.6 \cdot 10^8$	$1.6 \cdot 10^9$
preanodised + SnF ₂	80	$3.7 \cdot 10^9$	$4.6 \cdot 10^9$	79	$9.0 \cdot 10^8$	$1.7 \cdot 10^9$
preanodised + SnF ₂	88	$1.5 \cdot 10^9$	$2.2 \cdot 10^9$	89	$6.9 \cdot 10^8$	$1.3 \cdot 10^9$

Table 1: Values of B_C^{ac} , $Q(B_C^{ac})$ and $Q(0)$ at 1.5 K and 4.2 K of Nb₃Sn-resonators (TE₀₁₁, 9.7 GHz).



not preanodised

0,1 mm



preanodised

Figure 1: Nb₃Sn on Nb (111) – substrate (4h, 1050° C)

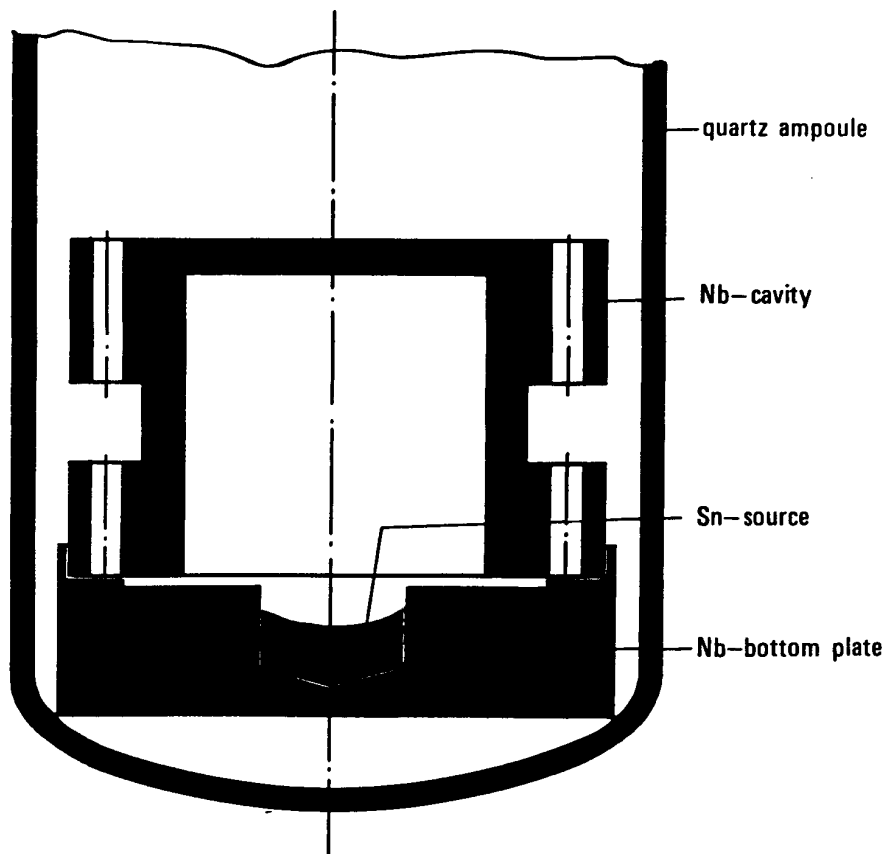


Figure 2: Arrangement for the preparation of Nb₃Sn cavities

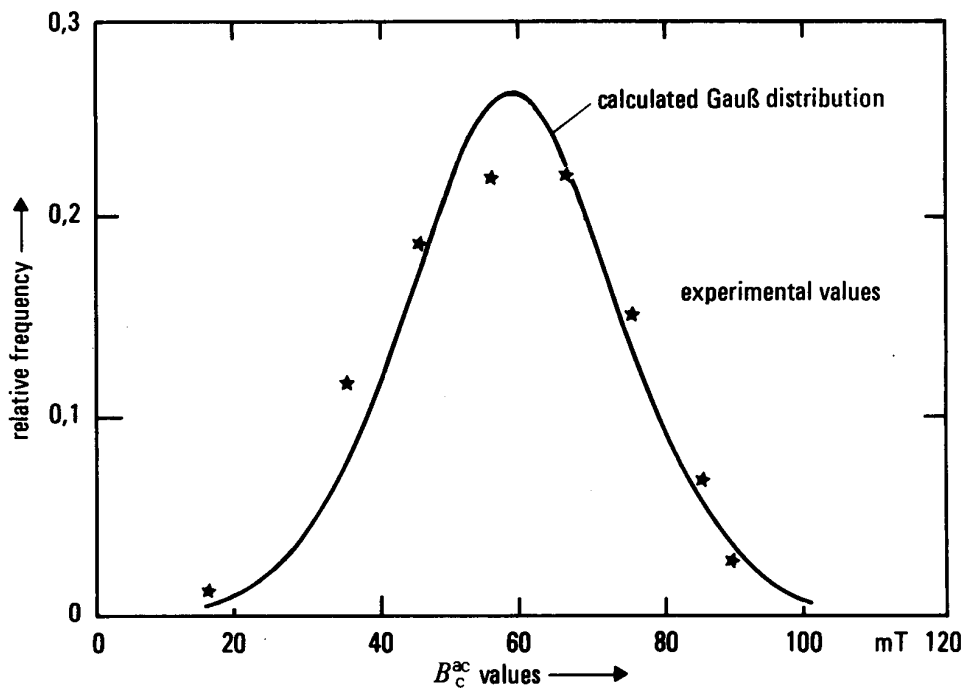


Figure 3: Distribution of measured B_c^{ac} - values (best results at 1.5 K for each preparation)

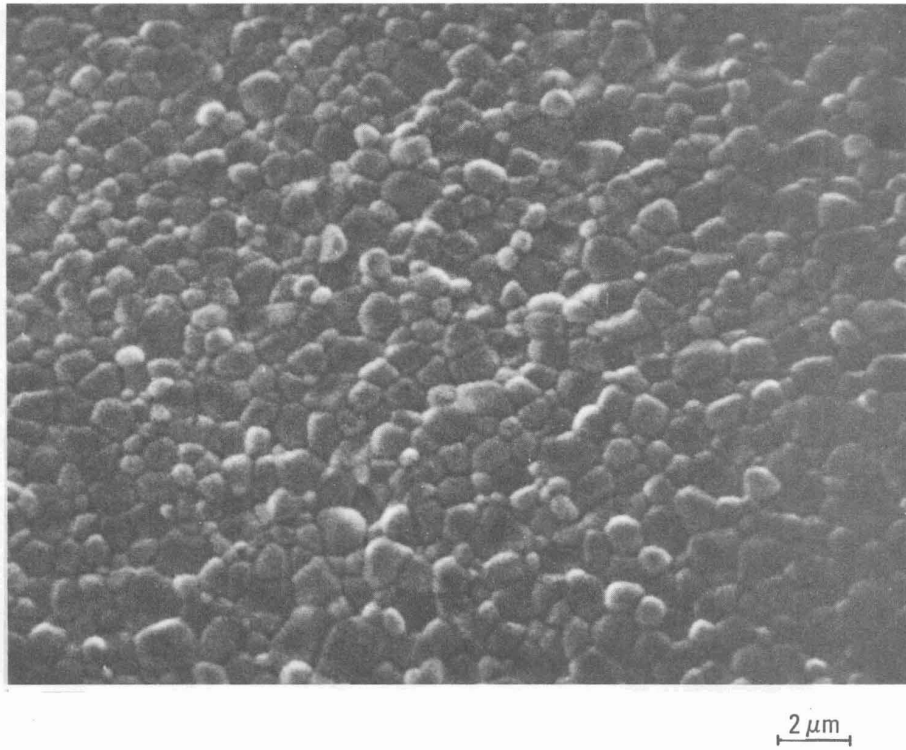


Figure 4: Nb₃Sn - layer on a Nb substrate (3h, 1050°C)

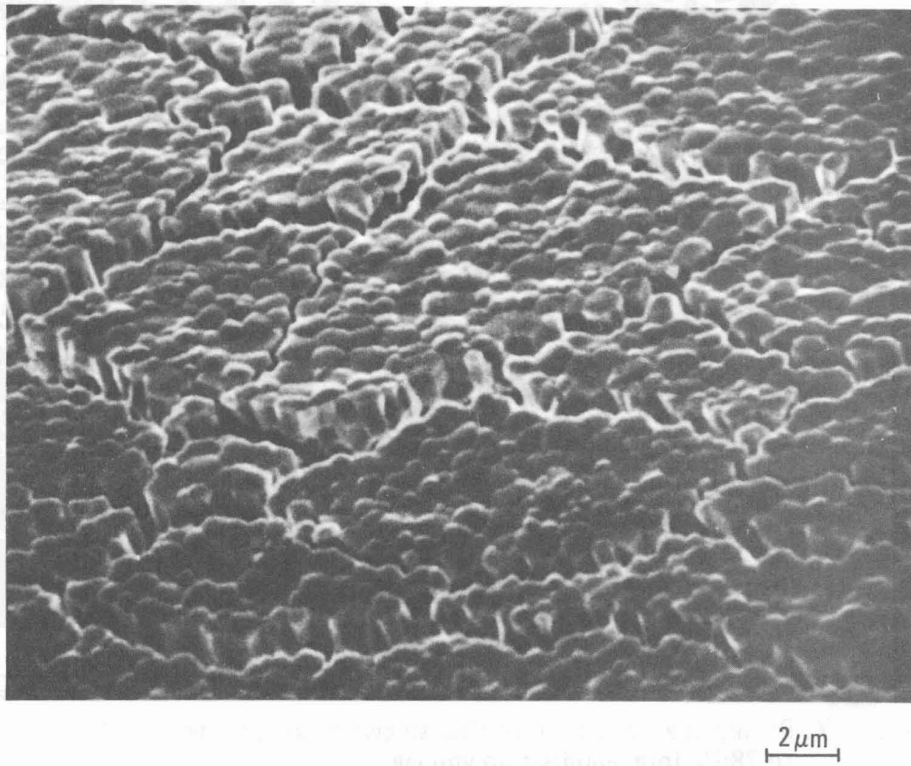


Figure 5: Intercrystalline fracture of a bent Nb₃Sn - layer on a Nb sheet

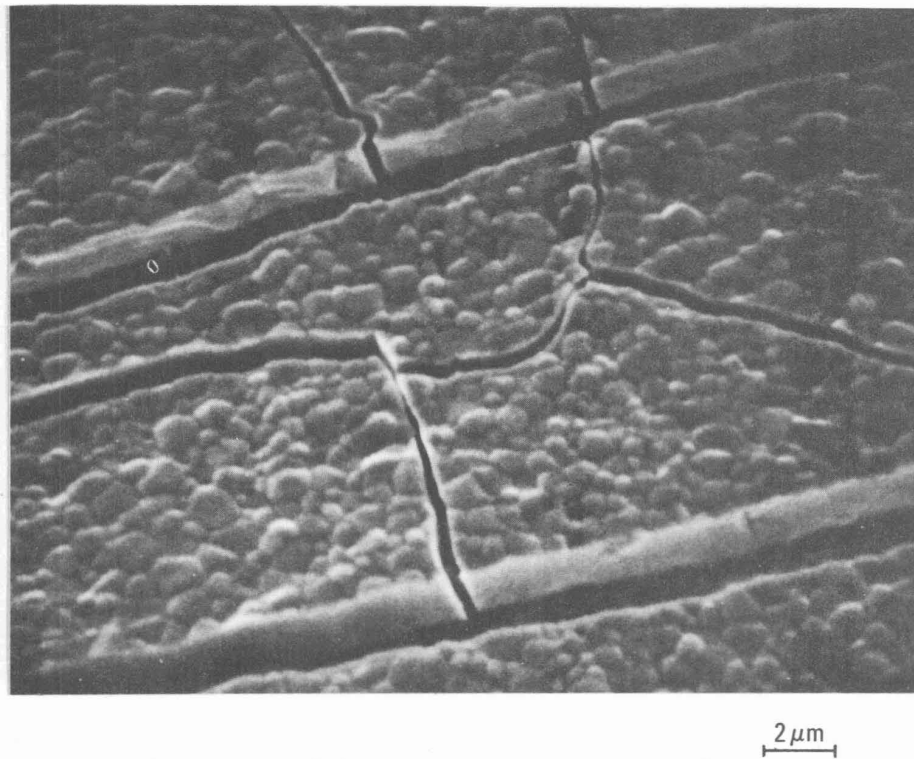


Figure 6: Transcrystalline fracture of a bent Nb₃Sn - layer on a Nb sheet

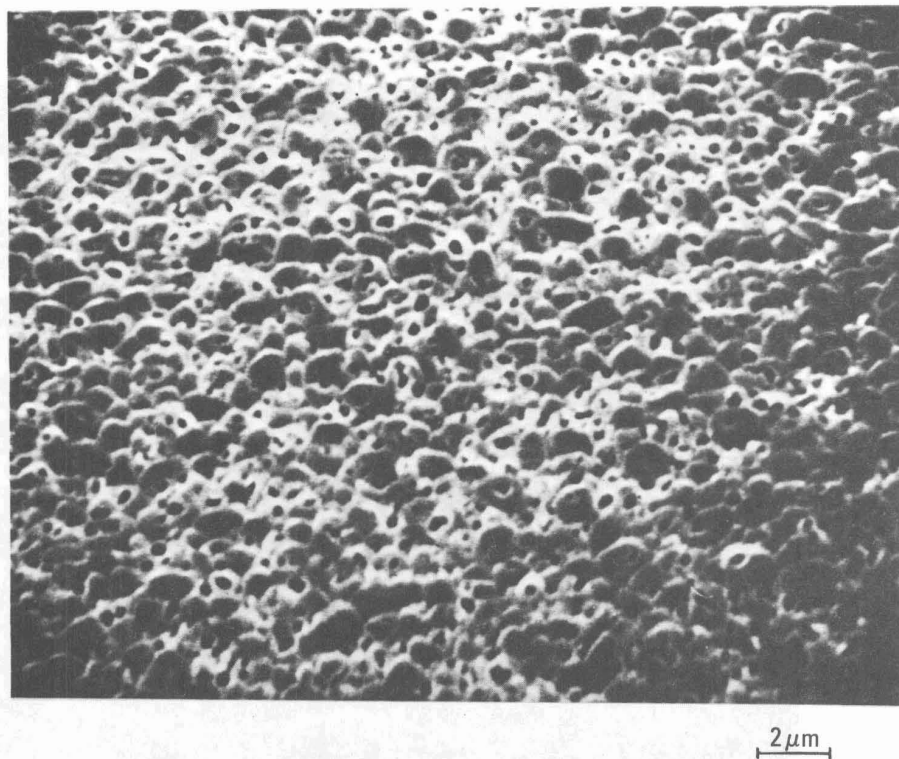


Figure 7: Pitting in a Nb₃Sn - layer after stepwise oxipolishing to 280 V total anodisation voltage