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# Electron microscopic examination of multifilamentary bronze-processed $Nb_3Sn$

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A detailed examination of the grain structure of commercial multifilamentary $N_3Sn$-wire has been carried out. This examination as well as the various electron microscopic preparation techniques used are discussed. Ion-milling was found to be a suitable method especially when combined with electrolytic pre-thinning. This yielded almost 100% acceptable samples. The grain size of the samples examined ranged from 30 to 200 nm. Based on the theory of normal grain growth an analytical description of grain growth versus reaction time, $t_R$, and reaction temperature, $T_R$, was determined and thus important parameters such as apparent activation energy, nucleation grain size and ultimate grain size of grain growth of $Nb_3Sn$ were obtained. The grain structure itself was found to be free of dislocations or other distortions whereas outstanding grain growth textures were evident, resulting in a certain grain size distribution over the $Nb_3Sn$ area. Strong evidence of abnormal grain growth of $Nb_3Sn$ grains was found depending on the heat treatment, for which some possible mechanisms are discussed. Based on the results of the analytical description of grain growth versus reaction conditions and an examination of the corresponding superconducting properties a "two-stage" annealing process is proposed which hypothetically should result in improved superconducting properties in the high-field range. Initial orientation examinations seem to confirm this hypothesis.

## 1. Introduction

The influence of microstructure on the superconducting properties of multifilamentary bronze-processed $Nb_3Sn$ conductors has been investigated by several authors [1–4]. It is well established that flux pinning in A15-superconductors is mainly caused by the interaction of flux lines with grain boundaries. Therefore the $Nb_3Sn$ average grain size, $d$, has been correlated to the maximum volume pinning force, $F_{p,\max}(d)$. It has been shown, that $F_{p,\max}$ increases monotonically with decreasing grain diameter for the size range investigated, i.e. from about 80 nm to 1 $\mu$m. For smaller grains only a few experimental results exist. Some of these [2, 4] seem to indicate that there is a maximum of the $F_{p,\max}(d)$ dependence. As this maximum is based on only one or two measured points in the small grain size region, its existence, so far, has not been demonstrated without doubt. A maximum is obviously to be expected if the grain size becomes smaller than the superconducting coherence length. The question of a maximum in the $F_{p,\max}(d)$ behaviour can only be answered by a thorough investigation of the grain structure for $d < 80$ nm. In addition, little information exists about the dependence of grain size on the reaction temperature, $T_R$, and time, $t_R$. The few results known from earlier publications are generally insufficient to analytically describe grain growth in diffusion reacted $Nb_3Sn$.

For these reasons, an extensive investigation of the grain and layer growth dependence on the reaction conditions has been undertaken. The results were correlated with the superconducting parameters and are discussed elsewhere [5]. A total number of 35 samples, all from the same

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production charge, has been investigated, with $t_R$ varying from 4 to 200h and $T_R$ from 570 to 800° C. Grain size ranged from 30 to 210 nm. For the region of main interest, $d < 80$ nm, the results for 16 samples gave some evidence of saturation of the $F_{p,\max}(d)$ behaviour at $d < 40$ nm, yet no maximum has been found [5]. Thirty-five samples was a sufficiently large number to make it possible to fit the grain growth results $d(t_R, T_R)$ to an existing theory [6].

The purpose of this paper is to give a brief description of the preparation techniques for the scanning electron microscope (SEM) and transmission electron microscope (TEM) studies and to discuss in detail the grain structure and grain growth results for bronze-processed multifilamentary $Nb_3Sn$.

## 2. Experimental details

### 2.1. Sample specification

The samples used for this investigation are characterized as follows: Commercial $Nb_3Sn$ bronze-processed multifilamentary wire of 0.38 mm outer diameter containing 1159 Nb-filaments of 5 $\mu$m diameter embedded in a Cu–13.5 wt% Sn matrix. A cross-section of the wire is shown in Fig. 1. Thirty-five samples have been reacted at different conditions to form a $Nb_3Sn$ layer of 0.1 to 2.5 $\mu$m thickness and grains of about 30 to 200 nm average diameter. The above wire specifications are suitable to satisfy the demands of electron microscopic preparation techniques.

### 2.2. Preparation techniques for electron microscope studies of the grain structure

In general, four different methods can be used to prepare samples for electron microscope (EM) investigations: (1) high resolution replicas (preparation for TEM); (2) surface preparation for SEM; (3) electrolytical thinning (preparation for TEM); and (4) ion-thinning (preparation for TEM). All of these methods have been studied extensively to test their suitability for $Nb_3Sn$ EM sample preparation. A detailed description of the methods, their advantages and drawbacks is given elsewhere [7]. In the following, only the successful techniques used to obtain the results discussed below are briefly discussed.

### 2.3. Preparation method for the measurement of the $Nb_3Sn$ area

To determine the $Nb_3Sn$ critical current density the reaction area was measured using SEM: Samples were embedded in resin, ground and mechanically polished parallel to the wire cross-section. Chemical etching then revealed the $Nb_3Sn$ area. Two etchants were found to be well suited: (1) 8% hydrous solution of $NH_4F$ at 70 to 80° C for 5 to 20 min; and (2) 9% HF (40%): 9% $H_2SO_4$ (conc.): 9% $H_2O$ (dist.): 1% $H_2O_2$: 72% lactic acid, for 10 to 30 sec at 10 to 20° C.

For samples with a very small $Nb_3Sn$ area, gold covering was required to increase the contrast. In addition, a replica technique was used to

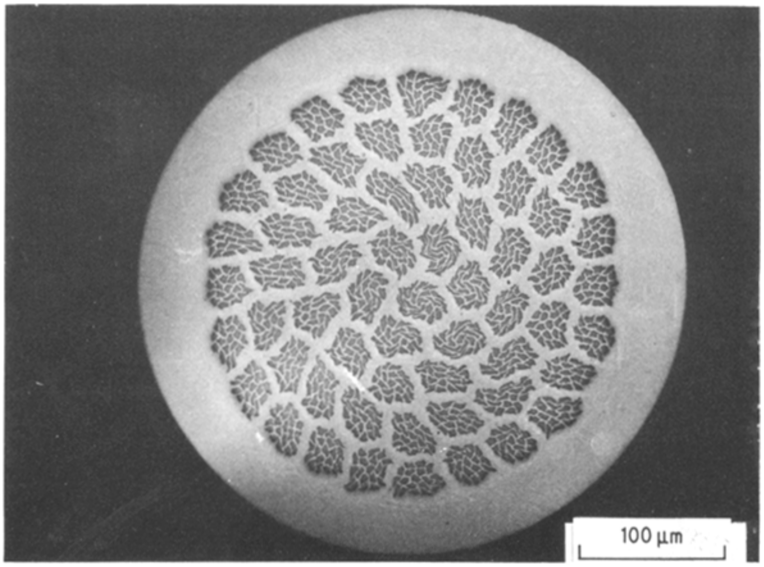

*Figure 1* Cross-section of the commercial multifilamentary wire investigated.

measure the $Nb_3Sn$ reaction area. This technique was found to be suitable for samples with grains larger than about 80 nm and gave results in good agreement with those obtained using SEM [7].

## 2.4. Preparation method for the measurement of the average grain size

For the determination of $Nb_3Sn$ average grain size all of the EM preparation methods mentioned at the beginning have been studied extensively. The following conclusions were drawn [7]:

(1) High resolution replica techniques as well as SEM were found not to be appropriate for examining $Nb_3Sn$ with average grain diameters less than 200 nm, as grains less than about 100 nm cannot be resolved. This is partially due to the composite structure of the material as well as to the delicate chemical behaviour and band emission of secondary electrons of $Nb_3Sn$. For grain diameters greater than 200 nm however both methods can be used successfully. As almost all of our samples have grains less than 200 nm, both methods have been rejected for our investigation.

(2) Electrolytic thinning proved to be inadequate due to the small differences in thinning velocities for the matrix and core material. Nevertheless, it was used as a pre-thinning technique which allowed ion-thinning to start at thicknesses less than 5 to 10 $\mu$m.

(3) Ion-thinning was found to be the only suitable method for preparing $Nb_3Sn$ for EM investigations. It has been combined with electrolytic pre-thinning.

## 2.5. Ion-thinning as a preparation method for TEM

The rotating sample target is hit by accelerated argon ions at small angles and is thus sputter-thinned. As the thinning velocity is low ($\approx 1\ \mu m\ h^{-1}$) the initial sample thickness must be small ($\approx 5$ to $10\ \mu m$). Difficulties that arise from preferential attack of different materials are not as severe as in the case of electropolishing as a smaller angle leads to a more homogeneous thinning by means of favoured thinning of outstanding surface structures. Lowering of thinning angles, however, causes the thinning velocity to decrease. Therefore, a compromise between thinning angle, starting thickness and number of samples has to be found to obtain satisfactory results. In the case of $Nb_3Sn$ composite preferential attack of the CuSn matrix prevented the successful thinning of cross-sectional samples even at small angles, as the filaments fell out before being thin enough. For this reason only longitudinal sections have been examined. They were prepared by the following procedure:

Sections of the samples were galvanitically bundled to a thickness of about 3 mm, using a standard copper electrolyte, which increased the area of $Nb_3Sn$ and, therefore, enhanced the probability of obtaining thin areas by ion-thinning. The bundled specimens were then ground in a longitudinal direction until the wire sections could be seen on both sides. Slides of 3 mm diameter were then punched from the specimen, ground to a thickness of about 30 $\mu$m and electrolytically pre-thinned to 5 to 10 $\mu$m, using an electrolyte of 93% methanol: 2% HF: 5% $H_2SO_4$ at $-55°$ C and a voltage of about 30 V.

This pre-thinning resulted in a brilliant, smooth surface which was found to be necessary for subsequent ion-thinning when starting with thicknesses below 20 $\mu$m, since the smoothing effect of ion-thinning is much less effective than that of the electrolytic process. Following this the sample was ion-thinned to its final state.

When the grain diameter was less than about 80 nm small thinning angles (10° to 7°) were used to increase the acceptable area and to avoid the overlapping of several grain layers.

Using the above procedure nearly 100% of the samples proved to be satisfactory for examining the grain structure.

Fig. 2 shows an example of the $Nb_3Sn$ grain structure produced by this technique and gives an indication of the variation of grain size with varying reaction temperature, $T_R$, showing equi-axed grains for three different reaction conditions (800° C/48 h, 680° C/48 h, 600° C/200 h).

# 3. Grain structure results and interpretation

After ion-thinning the samples were examined by TEM, using a microscope with a 150 kV accelerating voltage (Jeol, JEM 150). At least 12 micrographs from each sample were interpreted using the linear line intercept method, with about 1200 to 2500 grains counted per sample. Thus, the mean statistical error of grain size could be kept as low as 6.5%, even for the smallest grains.

Grain size ranged from about 30 to 210 nm. Its dependence on reaction temperature, $T_R$, and time, $t_R$, is shown in Fig. 3. For an analytical description,

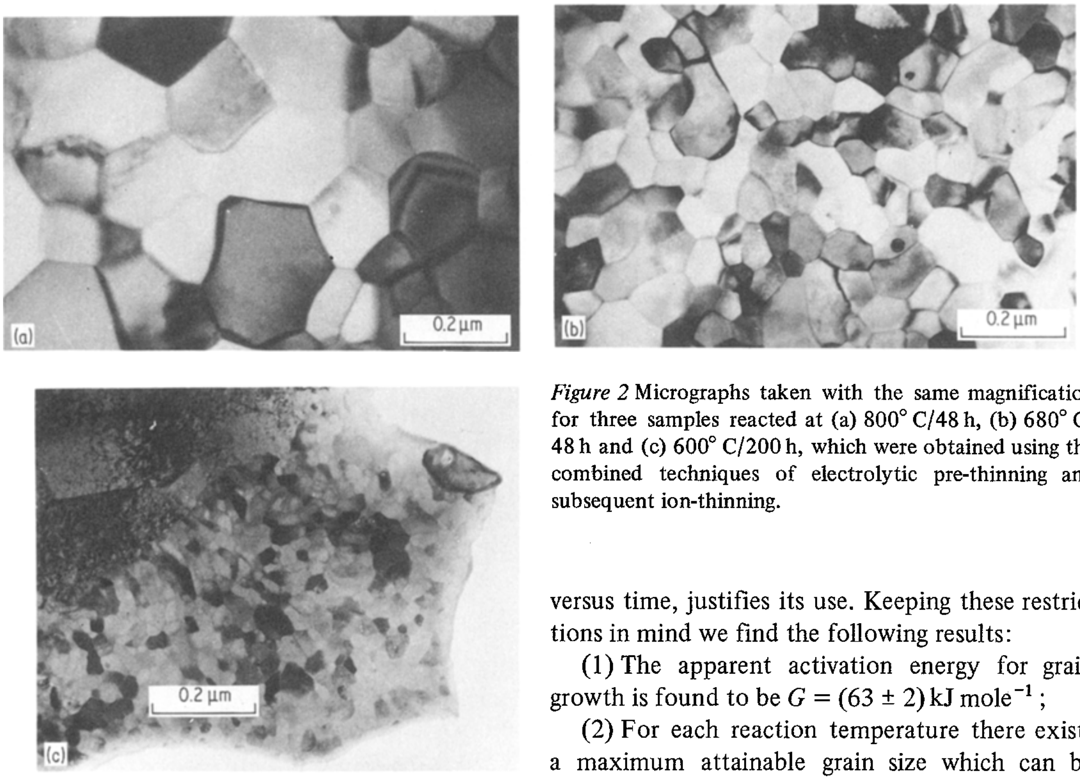

*Figure 2* Micrographs taken with the same magnification for three samples reacted at (a) 800° C/48 h, (b) 680° C/48 h and (c) 600° C/200 h, which were obtained using the combined techniques of electrolytic pre-thinning and subsequent ion-thinning.

grain growth can be separated into a product of a time and temperature contribution. The curves drawn in Fig. 3 are best fits to the function

$$d = \left[d_\infty - (d_\infty - d_0)\exp\left(-\frac{M}{d_\infty^2}\cdot t_\mathrm{R} - \frac{d-d_0}{d_\infty}\right)\right] \times \exp\left(-\frac{G}{RT_\mathrm{R}}\right) \quad (1)$$

where $d$ is the grain size in nm, $d_0$ is the grain size at time $t_\mathrm{R} = 0$, $d_\infty$ is the grain size for $t_\mathrm{R} \to \infty$, $G$ is the apparent activation energy for grain growth, $T_\mathrm{R}$ and $t_\mathrm{R}$ are the reaction temperature and time, $M$ is the grain boundary mobility and $R$ is the universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$). The time dependence of Equation 1 is used in the theory of normal grain growth [6].

Except for samples reacted at $T_\mathrm{R} = 750°\,\mathrm{C}$, grain sizes are well represented by the above function within the error limits, although it cannot be used strictly, as in its derivation the assumption is made that all the $\mathrm{Nb_3Sn}$ is already present at time $t_\mathrm{R} = 0$. This is obviously not the case. The fact however that most of the $\mathrm{Nb_3Sn}$ is formed in a short time (4 h at $T_\mathrm{R} = 800°\,\mathrm{C}$ and 24 h at 600° C) together with the slow variation of grain size versus time, justifies its use. Keeping these restrictions in mind we find the following results:

(1) The apparent activation energy for grain growth is found to be $G = (63 \pm 2)\,\mathrm{kJ\,mole^{-1}}$;

(2) For each reaction temperature there exists a maximum attainable grain size which can be written as

$$d_\infty = 2.59 \cdot 10^5 \cdot \exp(-G/RT_\mathrm{R}) \quad (\mathrm{nm}). \quad (2)$$

This yields $d_\infty = 225\,\mathrm{nm}$ at $T_\mathrm{R} = 800°\,\mathrm{C}$ and $d_\infty = 45\,\mathrm{nm}$ at $T_\mathrm{R} = 600°\,\mathrm{C}$.

(3) The nucleation of new $\mathrm{Nb_3Sn}$ grains takes place according to

$$d_0 = 1.58 \cdot 10^5 \cdot \exp(-G/RT_\mathrm{R}) \quad (\mathrm{nm}) \quad (3)$$

which yields $d_0 = 131\,\mathrm{nm}$ at $T_\mathrm{R} = 800°\,\mathrm{C}$ and $d_0 = 27\,\mathrm{nm}$ at $T_\mathrm{R} = 600°\,\mathrm{C}$.

(4) The ratio $M/d_\infty^2$ is $M/d_\infty^2 = 0.0232$.

These conclusions could be rather important regarding the $\mathrm{Nb_3Sn}$ formation reaction for commercial multifilamentary material. Measurements show that the critical current density in a medium transverse magnetic field ($b = B/B_{c2} \approx 0.3$, where $B$ is the transverse magnetic field and $B_{c2}$ is the upper critical transverse magnetic field) increases strongly with decreasing grain size [5]. At high fields however the refinement of microstructure shows no improvement of critical current density, as $B_{c2}$ as well as $T_c$ decrease when $T_\mathrm{R}$ is lowered. This degradation of superconducting properties is probably due to an atomic distortion of the A-15 structure which is obviously created to a larger extent at the low reaction temperature necessary

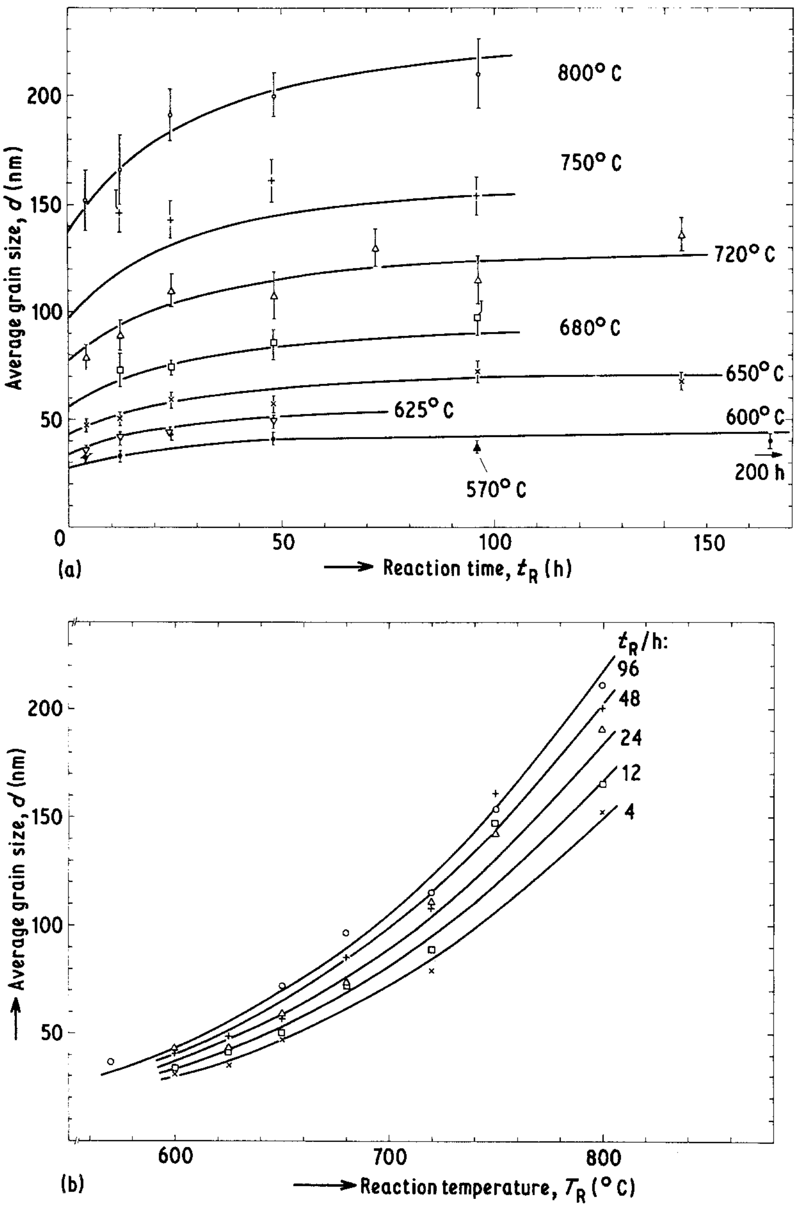

*Figure 3* (a) Reaction time and (b) reaction temperature dependence of $Nb_3Sn$ grain growth for the samples investigated. The drawn curves correspond to the fit described in the text.

to form a fine microstructure [8]. If one could succeed in healing these atomic distortions by a short heating to higher temperature without changing the grain size significantly, the accompanying increase of $T_c$ and $B_{c2}$ should lead to an increase of current density at high fields with decreasing grain size. Experiments using a sample reacted for 333 h at 500° C showed an increase of $T_c$ from 15.6 to 18.1 K (99% onset) when being heated at 810° C for 3 min. Using the above function a grain size of 15.1 nm can be calculated for this sample before the short heating and this should be increased to only 19 nm when annealed for 3 min at 810° C and to 32 nm when a practicable annealing time of about 25 min is applied. Such a fine microstructure, combined with the corresponding high critical data, should lead to enhanced values of the critical current density even at high fields. Moreover, as on annealing atomic defects are swept up by the migrating boundaries, the resulting complication of the grain boundary structure could yield an additional pinning effect and thus further increase the critical current density. A recent investigation clearly demonstrates the advantage of this two-stage reaction [5].

As a result of our TEM experiments the structure of the $Nb_3Sn$ layer can be divided into three

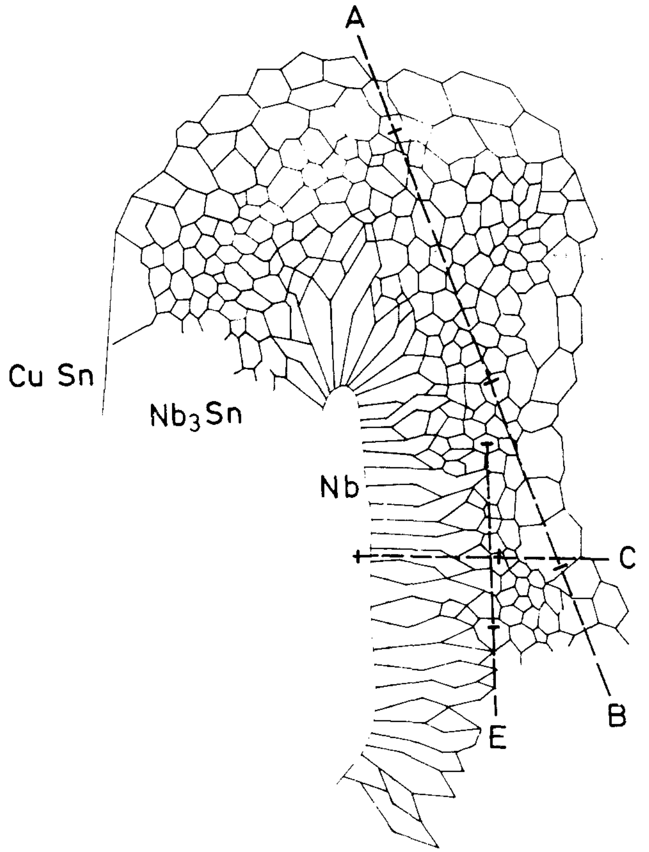

*Figure 4* Schematic view of the structure of the $Nb_3Sn$ area. The information contained in it was distilled from the results of all the various preparation techniques and is consistent with them. The various micrographs presented in this paper are roughly a vertical view to the lines drawn in this picture (longitudinal section!): line sections A and E correspond to Fig. 2a and b; line section B approximately corresponds to Fig. 6; and line section C corresponds to Fig. 5.

regions (see also Fig. 4): the $Nb_3Sn$ grows in a strongly radial textured, often columnar structure at the Nb side (Fig. 5); this columnar structure is often followed by a layer of equi-axed grains with a relatively homogenous grain size increasing slightly towards the CuSn side (Fig. 2); at the outer periphery the layer consists of one or two layers of very large grains, the diameter of which exceeds that of the other regions by a factor of 4 to 10 (Fig. 6). These grains were excluded when the average grain size was determined. These properties all depend on $T_R$. The columnar structure and the large outergrains are more pronounced at high $T_R$.

The observed structure can be understood as follows: With respect to the high degree of deformation the nucleating $Nb_3Sn$ is assumed to show strong orientation textures (which has been shown previously for $V_3Ga$ [9]). This orientation texture and the accompanying low specific interfacial energy of the grain boundaries for neighbouring columns together with their small mobility [6] leads to a negligible growth of the grains in the direction parallel to the Nb–$Nb_3Sn$ interface. On the other hand, the nucleating grains grow into the Nb thus resulting in a columnar shape. The resulting grain boundaries should possess a different structure, depending on whether they separate neighbouring columns or grains in a radial direction. This different structure became clearly visible using direct replica techniques (different chemical etching) and also by the different behaviour of the grain boundary contrast using TEM.

The observed large grains at the periphery of the $Nb_3Sn$ layer can be the result of *abnormal grain growth*, being initiated by two possible mechanisms:

(1) Due to the large number of deformation and intermediate annealing steps in the bronze-process, $Nb_3Sn$ is already formed before the final reaction treatment [2]. This was also the case with the wire used for our investigations; unreacted samples had a $T_c$ of 11.5 to 15.4 K. The grains of this $Nb_3Sn$-layer may exceed the nucleation diameter for the subsequent heat treatment if the temperature of intermediate annealing was chosen too high. This could be caused by the repeated cycle of annealing and deformation, that is, the formation and breaking of $Nb_3Sn$-layers. Thus the required conditions for abnormal grain growth are

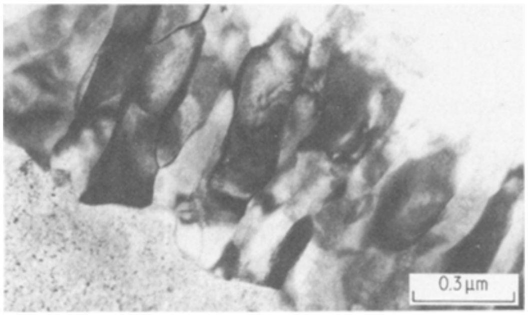

*Figure 5* Section vertical to the Nb–$Nb_3Sn$ interface showing columnar growth of the $Nb_3Sn$ on the Nb side.

already present before the final annealing, as normal grain growth requires a limitation of the size distribution of the growing grains [6]. On annealing the grains already present now grow *abnormally*, with a nearly linear time law, in contrast to the curves shown in Fig. 3. Thus these grains grow far more rapidly than the nucleating ones, resulting in an even more broadened grain size distribution which in turn intensifies abnormal grain growth. Abnormal grain growth only ceases when the whole $Nb_3Sn$ layer is consumed by the abnormally grown grains, thus resulting in a narrower grain size distribution. At any intermediate stage of this process the resulting grain structure is a duplex one: regions of very large (abnormally grown) grains change with regions of small (normally grown) grains (Fig. 6).

(2) A second possible mechanism for abnormal grain growth arises from the orientation texture of the nucleating $Nb_3Sn$ grains, which allows some grains lying within a certain favourable orientation range with a correspondingly high grain-boundary energy to grow abnormally [6]. The resulting structure thus also possesses a strong orientation texture which in general is different from the former orientation texture but is determined by it. This mechanism should start near the Nb–$Nb_3Sn$ interface.

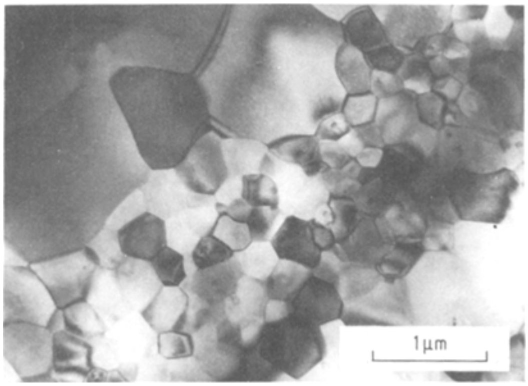

*Figure 6* Micrograph taken along the outer periphery of the $Nb_3Sn$ layer clearly showing the existence of very large grains compared with the average grain size in this area. The picture corresponds to line section B of Fig. 4.

Indeed using replica techniques a different chemical behaviour could often be seen between the inner and outer regions of the $Nb_3Sn$ [7]. Thus the existence of textures in the inner, as well as the outer, regions of the $Nb_3Sn$ area is rather probable.

These results should be considered with respect to their effect on the superconducting properties: as the grain boundaries act as pinning sites the possible change of the grain structure from a very fine one to a rather coarse one, which is uncontrollable and can occur very quickly compared with usual annealing times, would result in a drastic dilution of pinning centres and thus considerably alter superconducting properties (i.e. reduce critical current densities). As the conditions for abnormal grain growth are a result of wire fabrication this can even lead to unreproducable superconducting properties even when using wires with identical specifications, but from different charges, which would be rather crucial with respect to magnet fabrication.

It should be mentioned that the risk of abnormal grain growth becomes increasingly negligible when the final annealing temperature is lowered, as abnormal grain growth is strongly dependent on the reaction temperature [6].

Both of the mechanisms of abnormal grain growth mentioned are clearly based on the fabrication condition of the specific wire (deformation and intermediate anneal) and so are the resulting superconducting properties. Partial deviations concerning the superconducting properties in correlation with average grain size from different authors [1–5] might thus be due to a different $Nb_3Sn$ grain structure morphology.

Besides the investigation of grain structure morphology special interest was given to the occurrence of crystal defects within the $Nb_3Sn$, as strong pinning of grain boundaries might be caused by precipitates within them. Our investigations which were partially carried out using dark-field TEM techniques showed neither dislocations in the inner regions of the grains or at the boundaries nor any indication of precipitation. Excluding point defects which could not be examined as ion-thinning produces many point defects itself, the $Nb_3Sn$ structure thus appears to be completely undistorted. Precipitates should therefore be extremely small (≈ 2 to 4 nm) and would also have to be of coherent character.

## 4. Conclusion

It has been shown that ion-milling seems to be the only favourable method for preparing small grain $Nb_3Sn$ material for electron microscopic examination of grain size, whereas replica techniques, as well as SEM techniques, are only suitable for examination of growth of $Nb_3Sn$ area or for studying large grain material.

Starting with a grain size of 210 nm, this can be lowered to 30 nm by altering the reaction conditions. All samples fitted a theoretical curve of grain growth versus reaction temperature and reaction time well in terms of apparent activation energy, nucleation grain size, ultimate grain size and grain boundary mobility, thereby making it possible to calculate these quantities.

Extrapolating this fitted curve to lower reaction temperatures and longer reaction times permits a rough calculation of grain size for very low reaction temperatures, for which no grain sizes have actually been measured yet. Based on the supposition that this analytical description is valid for reaction temperatures of about 500° C it was shown that a "two-stage" annealing process which uses a very long diffusion reaction time at low reaction temperatures (stage one), followed by a short heating for a few minutes at high temperatures (≈ 800° C, stage two), results in a very fine $Nb_3Sn$ grain structure which eventually possesses far better superconducting properties at higher magnetic fields than otherwise previously obtained. This is caused by the prevention of high atomic disorder and eventually by additional pinning effects. Initial investigations seem to confirm this hypothesis.

The $Nb_3Sn$ layer itself was found to be free of any dislocations or other defects, but strongly textured. Evidence was found that abnormal grain growth takes place under certain circumstances especially at the outer periphery of the $Nb_3Sn$ area. This is probably due to the fabrication process of the wire and can perhaps be prevented by using lower intermediate annealing temperatures.

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