

CHARACTERISTICS OF A PRODUCTION ROUTE FOR FILAMENTARY Nb_3Sn SUPERCONDUCTORS BASED ON A REACTION BETWEEN NIOBIUM AND Nb_6Sn_5

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Summary

Monofilamentary Nb_3Sn superconductors have been made by application of a reaction between Nb_6Sn_5 powder and niobium. The layer thickness of Nb_3Sn shows a parabolic time dependence, implying diffusion-controlled layer growth. The activation energy for diffusion is 268 kJ mol^{-1} . The critical temperature T_c is about 17.5 K and the overall critical current density J_c is about $5 \times 10^8 \text{ A m}^{-2}$ at 8 T, both after annealing at 675°C . These values are comparable with those obtained for so-called ECN-type superconductors, which are based on a reaction between NbSn_2 powder and niobium. An advantage of the use of Nb_6Sn_5 powder in comparison with NbSn_2 is the kinetics of growth of Nb_3Sn , which allows a lowering of the reaction temperature to $600\text{--}625^\circ\text{C}$ for filament diameters of about $30 \mu\text{m}$.

1. Introduction

Over the past 30 years the superconducting compound Nb_3Sn has gained much interest for application in high field magnets, for which a multifilamentary configuration is required. However, Nb_3Sn is a very brittle material which cannot be shaped into this configuration. Therefore, multifilamentary Nb_3Sn superconductors are manufactured in two subsequent stages, consisting of multifilament wire manufacturing (comprising only formable components) followed by a heat treatment in order to form the superconducting Nb_3Sn . The most well-known production route, the bronze process [1], starts from pure niobium and tin-poor α -bronze (7 at.% Sn), which are both ductile materials. By heating at around 700°C , the niobium and bronze form a Nb_3Sn diffusion layer at their interface.

The ECN process [2] and the solid-liquid diffusion method [3] are based on a reaction between relatively tin-rich mixtures and niobium. The ECN process, for instance, concerns a reaction between an $\text{NbSn}_2\text{-Cu}$ powder mixture and niobium. According to the description of the reaction phenomena in an ECN-type wire [4],

the non-superconducting phase Nb_6Sn_5 is formed as an intermediate step. In a later stage this Nb_6Sn_5 decomposes and Nb_3Sn is formed in both a fine-grained and a coarse-grained morphology. According to a previous investigation [5], the microstructure in ECN-type wires is the result of decomposition of Nb_6Sn_5 in combination with tin being the more mobile species in Nb_3Sn . This leads to two nucleation sites and, for that reason, two different grain sizes for Nb_3Sn . Since the grain boundaries in Nb_3Sn are important for obtaining high current densities [1], coarse grains are not favourable in this respect. Besides, many crevices and pores have been observed in the coarse-grained phase [4], which are most probably detrimental for the strain sensitivity as they may act as stress concentrators. Therefore further research of the ECN method aims at the realization of an entirely fine-grained microstructure.

From our previous investigation [5], it appears that, starting from NbSn_2 , prevention of the formation of Nb_6Sn_5 by destabilization of this phase is a possible method to arrive at fully fine grained Nb_3Sn . A more straightforward possibility is to start from a Nb_6Sn_5 powder core instead of NbSn_2 .

Following the latter proposal, Nb_3Sn superconductive wire was made by applying Nb_6Sn_5 powder as a tin source. The properties of this wire were investigated, focusing on the microstructure, the reaction kinetics and the superconductivity.

2. Experimental details

All experiments were performed on monofilamentary wires which were made in the following way. An axial hole of diameter 1.5 mm and length 25 mm was drilled in niobium rods (purity, 99.9%) of diameter 4.5 mm and length 100 mm.

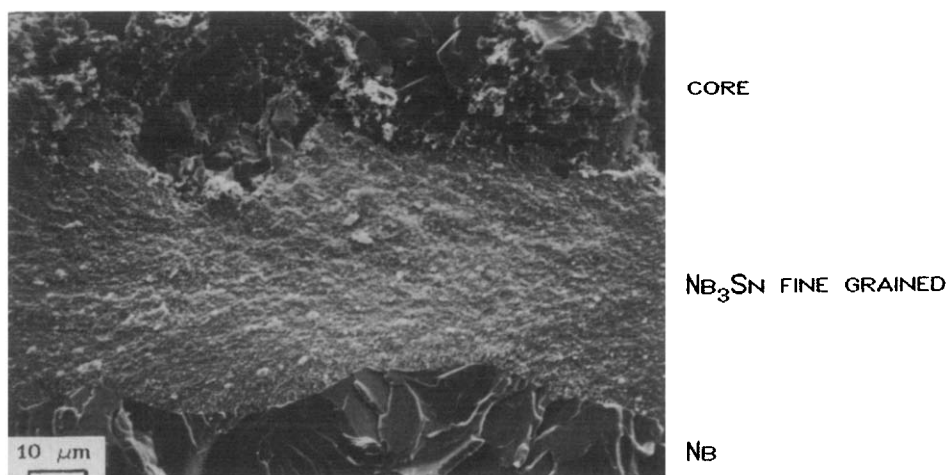


Fig. 1. Fracture surface of the reaction layer in a monofilamentary wire with a Nb_6Sn_5 -10wt.%Cu powder core after 408 h at 675 °C. The reaction layer consists of fine-grained Nb_3Sn .

The holes were filled with a powder mixture of Nb_6Sn_5 and 10 wt.% Cu, and closed with a niobium plug. The niobium rods were then placed inside a copper tube of outside diameter 6 mm and cold drawn to a diameter of 0.69 mm. At this size the powder core has a diameter of around $180\ \mu\text{m}$. Prior to heat treatment, lengths of 80 mm were cut from the wires and encapsulated under vacuum in silica. After heat treatment, the samples were quenched in water and transverse sections were taken both by cutting and by fracturing under liquid nitrogen. The latter samples were used for determination of the microstructure of the fracture surface by scanning electron microscopy. The former samples were prepared for electron probe microanalysis and for measurement of the layer thickness with a calibrated optical micrometer.

Short samples about 30 mm in length were used for measurement of the critical temperature T_c and the critical current density J_c . In both cases a resistive four-probe technique was used. For T_c measurement a sample current of 10 mA was used and the temperature was measured with a calibrated germanium thermometer.

3. Results

3.1. Morphology and kinetics

Figure 1 shows a micrograph of the structure of a fully reacted wire with a Nb_6Sn_5 -10wt.%Cu powder core. For comparison, a micrograph of a similar sample using a NbSn_2 -10wt.%Cu powder core is shown in Fig. 2. In the latter case both fine- and coarse-grained Nb_3Sn are formed, whereas in the former case only fine-grained Nb_3Sn is observed. The composition of Nb_3Sn for various annealing conditions is given in Table 1.

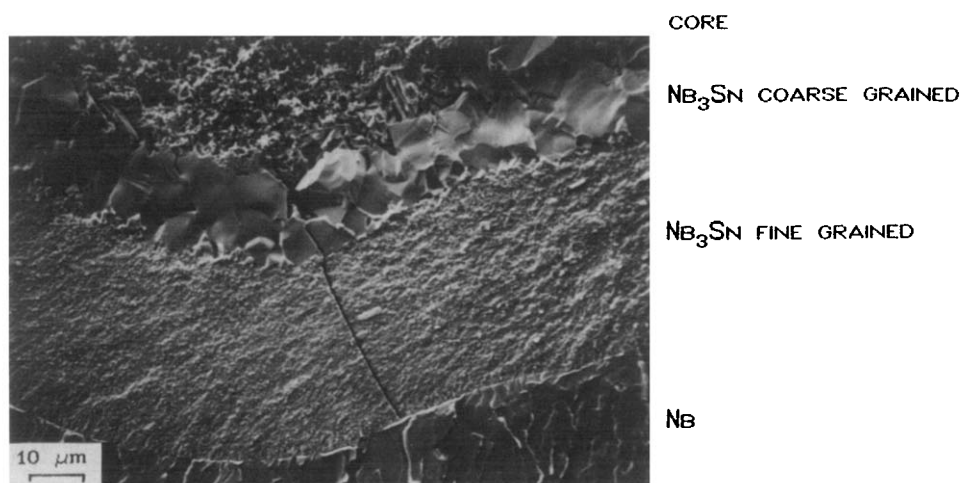


Fig. 2. Fracture surface of the reaction layer in a monofilamentary wire with a NbSn_2 -10wt.%Cu powder core after 408 h at $675\ ^\circ\text{C}$. The reaction layer consists of fine- and coarse-grained Nb_3Sn .

TABLE 1

Composition of fine-grained Nb₃Sn in monofilamentary wires with a Nb₆Sn₅-10wt.%Cu powder core for various heat treatments (the data are averaged over five or more random measurements)

Heat treatment condition (h/°C)	Composition of fine-grained Nb ₃ Sn		
	Nb (at.%)	Sn (at.%)	Cu (at.%)
504/625	75.86	22.94	1.20
288/660	76.09	22.62	1.29
336/675	76.34	22.86	0.81
336/675	76.00	23.37	0.64
456/675	75.65	23.64	0.71
504/675	76.23	23.01	0.76
504/675	76.11	23.19	0.71
96/725	76.19	23.55	0.27

The squared layer thicknesses as a function of annealing time are given in Fig. 3 for wires with a Nb₆Sn₅-10wt.%Cu powder core. Without copper the layer growth proceeds much slower (about 650 h at 675 °C for full reaction) although a similar ultimate thickness is obtained. A least-squares fit of the data of Fig. 3 for layer widths up to 30 μm reveals a straight line, implying diffusion-controlled parabolic layer growth. Beyond a layer thickness of 30 μm further growth at a lower rate has been observed at 675 and 725 °C. The linear sections in Fig. 3 can be expressed as

$$d^2 = k(t - t_0) \quad (1)$$

where d is the layer thickness, k is the penetration constant, t and t_0 are the time and incubation time respectively.

The regression data are given in Table 2. Since layer growth is governed by diffusion the chemical diffusion coefficient can be calculated. The values are included in Table 2. Details of the calculation are given in Appendix A. According to the well-known Arrhenius expression for the temperature dependence of the diffusion coefficient D we may write

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \quad (2)$$

where D_0 is the frequency factor, Q is the activation energy, R is the gas constant (8.31 J (mol K)⁻¹) and T is the absolute temperature.

The activation energy Q and the frequency factor D_0 follow from a least-squares estimation of $\ln D$ as a function of reciprocal temperature (Fig. 4)

$$Q = 268 \text{ kJ mol}^{-1}$$

$$D_0 = 1 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$$

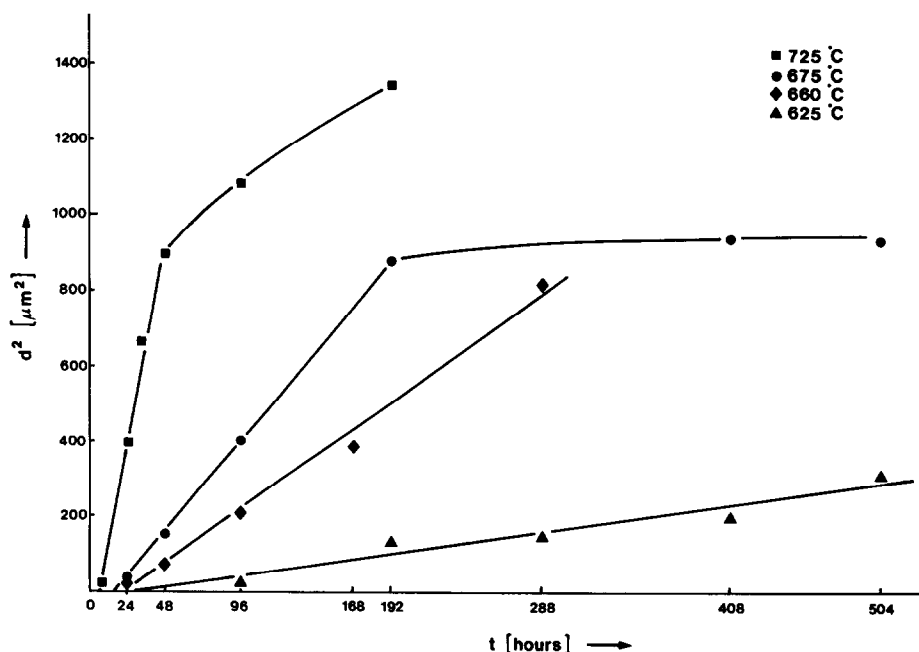


Fig. 3. Squared layer thicknesses vs. time of fine-grained Nb_3Sn formed in monofilamentary samples with a Nb_6Sn_5 -10wt.%Cu powder core (about $180 \mu\text{m}$ in diameter) and heat treated at various temperatures.

TABLE 2

Regression data of fine-grained Nb_3Sn layer thickness in monofilamentary wires with Nb_6Sn_5 -10wt.%Cu powder cores, according to eqn. (1), and chemical diffusion coefficients calculated from eqn. (A5).

Annealing temperature (°C)	Incubation time, t_0 (h)	Penetration constant, k ($\text{cm}^2 \text{s}^{-1}$)	Correlation coefficient R	Chemical diffusion coefficient, D ($\text{cm}^2 \text{s}^{-1}$)
625	31.20	1.69×10^{-12}	0.9650	2.3×10^{-12}
660	23.84	8.33×10^{-12}	0.9956	1.1×10^{-11}
675	16.31	1.39×10^{-11}	0.9999	1.9×10^{-11}
725	6.83	6.33×10^{-11}	0.9912	8.6×10^{-11}

3.2. Superconducting properties

In order to get an impression about the superconducting properties of the wires, T_c and J_c were measured for various heat treatment conditions. Figure 5 gives the critical temperatures. Obviously T_c does not depend on annealing time, but appears to increase with increasing annealing temperature.

Figure 6 gives the overall critical current density as a function of magnetic field. The data should be interpreted as indicative, because the greater part of the

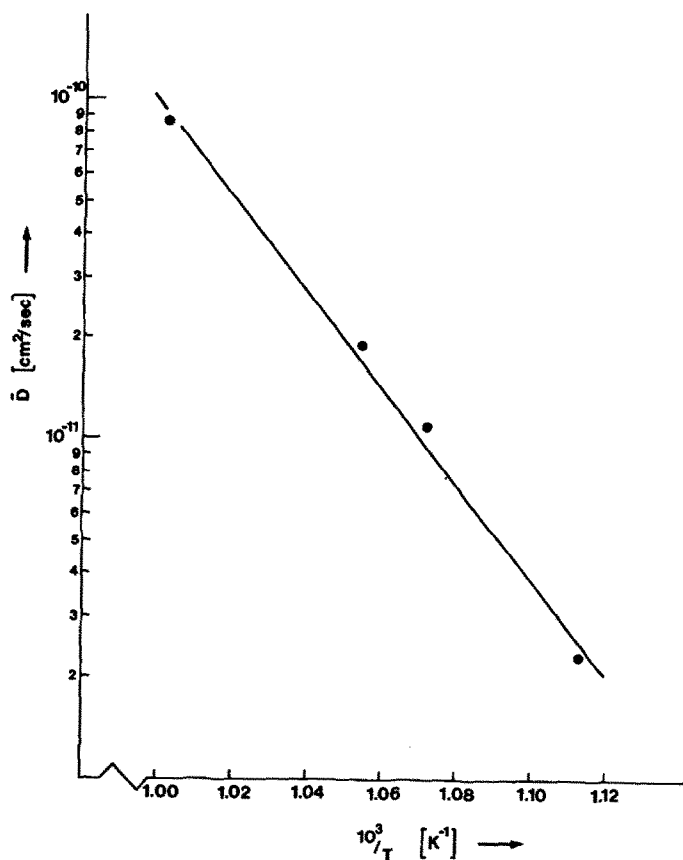


Fig. 4. Chemical diffusion coefficient of Nb_3Sn as a function of reciprocal temperature. The line represents the relation.

$$D = 1.0 \times 10^4 \exp\left(\frac{-268000}{RT}\right)$$

measurements showed current sharing prior to the transition to normal conductivity. J_c was determined as the current level at +1.5 μV from the transition point.

4. Discussion

4.1. Microstructure

The difference in microstructure between Nb_3Sn layers formed from $NbSn_2$ and Nb_6Sn_5 powder can be explained by the mechanism of formation (also see ref. 5). During the reaction of Nb_6Sn_5 and niobium, Nb_3Sn is formed by two different mechanisms: one is the decomposition of Nb_6Sn_5 , leading to relatively large grains (5–15 μm), the other is the reaction between tin and niobium which leads to very small grains (less than 0.1 μm). If $NbSn_2$ powder is used as a starting material a

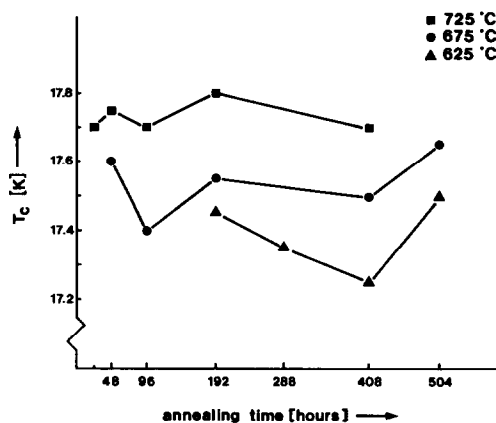


Fig. 5. Midpoint critical temperature (average of onset and offset T_c) of monofilamentary wires with a Nb_6Sn_5 -10wt.%Cu powder core dependent on heat treatment time and temperature.

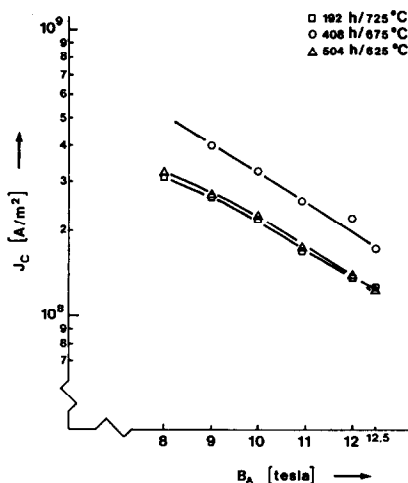


Fig. 6. Overall critical current density as a function of the applied magnetic field of monofilamentary wires with Nb_6Sn_5 -10wt.%Cu powder cores. Wire diameter is 0.69 mm.

Nb_6Sn_5 layer is formed prior to formation of Nb_3Sn . Decomposition of this layer consequently gives two different grain sizes (Fig. 2). Use of Nb_6Sn_5 powder as starting material results in direct growth of Nb_3Sn from tin and niobium according to the second mechanism. The porous and unsolid decomposition product remains in the core.

4.2. Layer growth kinetics

The observed parabolic layer growth (Fig. 3) shows that diffusion is rate controlling with constant boundary conditions. The requirement of a constant boundary condition is obviously fulfilled for the niobium. However, it is also fulfilled for the powder core, which can be seen from the equilibrium diagram of the Nb-Sn-Cu systems [6]. One should realize that at $t > 0$ Nb_3Sn has been formed in the powder core as a consequence of the decomposition of Nb_6Sn_5 . Therefore, the overall core composition is located in the three-phase field Nb_6Sn_5 - Nb_3Sn - γ -bronze. In a three-phase field all compositions and, hence, all activities are fixed. Thus tin is supplied from decomposition of Nb_6Sn_5 without a change in tin activity, until the overall composition of the powder core is shifted to the two-phase field Nb_3Sn - γ -bronze. From this moment on, supply of tin will lead to a decrease in the tin activity and slower kinetics may be expected. This is indeed observed for the wires heat treated at 725 and 675 °C.

In a previous article [5] Nb_3Sn layer growth proportional to $t^{0.75}$ has been reported. This behaviour has been explained by a combination of changing boundary conditions and relatively high diffusion velocities of tin in the Nb_3Sn layer. The high diffusivity of tin is explained as being due to the presence of a high diffusivity γ -bronze phase at the grain boundaries of Nb_3Sn [5]. The presence of

this bronze is due to the convex shape of the reacting niobium, which induces tensile stresses in a tangential direction during growth of Nb_3Sn , enabling the accumulation of bronze. A similar suggestion has been made for wires made according to the bronze process [1, 7, 8]. However, in the present case the shape of the reacting niobium is concave, resulting in compressive stresses which prevent accumulation of bronze at the grain boundaries. Thus the diffusion rate of tin is lower and layer growth is entirely governed by diffusion. This explanation is supported by the observed copper content of Nb_3Sn , which is significantly lower for the present experiments (less than 1 at.% for annealing at 675 °C, Table 1) than for the experiments with convex niobium substrates (about 3 at.% for annealing at 675 °C).

4.3. T_c measurements

Higher annealing temperatures lead to higher values of T_c (Fig. 5), which can probably be explained by the measured differences in composition. From Table 1 it can be seen that the composition of Nb_3Sn is closer to stoichiometry after annealing at higher temperature. As it is known from the literature [9] that T_c is maximal for defect-free stoichiometric phases, it can be concluded that the present results also follow this qualitative rule. The measured value of 17.5 K after 192 h at 675 °C agrees well with the value for ECN-type wires given by Veringa *et al.* [4], *i.e.* 17.7 K.

4.4. J_c measurements

The overall critical current density J_c and its field dependence for the superconductors manufactured with Nb_6Sn_5 powder is comparable with the reported values for 18-filament ECN-type superconductors [4]. A calculation shows that the intrinsic current density of Nb_3Sn made from Nb_6Sn_5 powder is about 25% higher than the current density of Nb_3Sn made from NbSn_2 . However, this advantage is compensated by the fact that the overall yield of Nb_3Sn is smaller by using Nb_6Sn_5 powder instead of NbSn_2 . The use of Nb_6Sn_5 powder has a definite advantage from the point of view of the kinetics of growth of Nb_3Sn . The faster kinetics enable a lowering of the reaction temperature to 600–625 °C for multifilament wire with a powder core diameter of about 30 μm , in order to arrive at the same overall critical current density as the NbSn_2 -core manufactured wires during the same annealing time at 675 °C.

5. Conclusions

(1) A fine-grained Nb_3Sn diffusion layer can be produced from a reaction between Nb_6Sn_5 -Cu powder mixtures and niobium. Nb_3Sn layer growth is controlled by diffusion if 10 wt.% Cu is added and a concave niobium substrate is used. The activation energy for diffusion is 268 kJ mol^{-1} .

(2) The critical temperature and the critical current density of Nb_3Sn made from Nb_6Sn_5 -Cu powder mixtures and niobium are comparable with those

obtained for Nb₃Sn produced from a NbSn₂-Cu powder core and niobium (ECN method).

(3) The kinetics of Nb₃Sn layer growth is faster if Nb₆Sn₅ powder is used, enabling the application of reaction temperatures between 600–625 °C for manufacturing multifilamentary wire.

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Appendix A

Calculation of the chemical diffusion coefficient of Nb₃Sn was done by following the method proposed by Heumann [A1], which comprises the simultaneous assumptions of a linear concentration profile and a constant D . This implies the existence of a steady state situation which is obviously not correct. Nevertheless, this approach is more often used to relate layer growth kinetics to the diffusion coefficient by allowing the profile to change with time [A2]. Since it is known that tin is the more mobile species in Nb₃Sn [5], growth of Nb₃Sn may be described by a mass balance for the interface between Nb₃Sn and niobium only

$$-D \frac{dc}{dx} = c_1 \frac{dx}{dt} \quad (\text{A1})$$

where: c is the tin concentration, c_1 is the concentration in Nb₃Sn at the interface with niobium, x is the instantaneous Nb₃Sn layer thickness and t is the time.

By applying the assumption of a linear profile this becomes:

$$-D \frac{c_1 - c_2}{x} = c_1 \frac{dx}{dt} \quad (\text{A2})$$

where c_2 is the tin concentration in Nb_3Sn at the interface with Nb_6Sn_5 .

Integration of eqn. (A2) between the incubation time t_0 and t and between $x=0$ and $x=d$ gives:

$$D = \frac{d^2}{2(t-t_0)} \frac{c_1}{c_2 - c_1} \quad (\text{A3})$$

If the molar volume is concentration independent we can substitute the molar fractions for the concentrations:

$$D = \frac{d^2}{2(t-t_0)} \frac{N_1}{N_2 - N_1} \quad (\text{A4})$$

If the local compositions at the interfaces between Nb_3Sn and Nb_6Sn_5 and Nb_3Sn and niobium correspond to the equilibrium concentrations, the homogeneity range according to the equilibrium diagram can be substituted into eqn. (A4). Since this interval is generally small, inaccuracies will give large errors in the calculated value of D . In the present case accurate data of the homogeneity range of Nb_3Sn are available at 1000 °C for the binary Nb–Sn system [A3]. This range is between 17.5 and 26 at.% Sn. An average value for the molar fraction of tin in the numerator was taken, *i.e.* 0.23. Thus, eqn. (A4) becomes

$$D = \frac{d^2}{t-t_0} 1.35 \quad (\text{A5})$$

References for Appendix A

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