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Superconducting Nb_3Sn Diffusion Layers

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In the present work an experimental apparatus for the production of Nb_3Sn superconducting ribbon is described. The fabrication method for these ribbons takes advantage of the diffusion process of tin into niobium. We give also some details of the technique by which the superconducting properties of Nb_3Sn have been tested. A number of preliminary experimental results are discussed with the purpose of pointing out the main fabrication parameters which influence the superconducting properties. Finally future developments of this research program are outlined.

1. Introduction

The superconducting intermetallic compound Nb_3Sn has shown itself to be a very useful material for the construction of solenoids especially for the 100 KOe region. Its various production methods are described in the literature [1-4] to which the reader is referred. In the present paper we discuss some preliminary results concerning the superconducting properties of Nb_3Sn ribbons obtained by diffusion of tin into niobium.

The microscopic mechanism through which the diffusion of molten tin into niobium takes place is not fully understood; recently however Old and MacPhail [5] have pointed out that the formation of the Nb_3Sn layer results from a solution-deposition mechanism super-imposed on the true diffusion process. The properties of the superconducting layer depend strongly on the reaction temperature and duration as well as on the surface state, purity and heat treatment of the niobium. Our results do not give the final requirements for a practical material and the main interest of this paper is concerned with the discussion of the dependence of the superconducting properties on the various parameters affecting the diffusion process.

We point out also that a reliable material must be stabilised against sudden transitions to the normal state. The theory of stabilisation is quite extensively known [6, 7], but practical methods for achieving good stabilisation could give rise to some serious technical problems. Our results are concerned with bare Nb_3Sn samples although we are currently testing different methods to stabilise the superconducting ribbon with suitable normal metals.

In section 2 we will describe the production apparatus and technique. Section 3 will be devoted to the measuring apparatus and technique while in section 4 we will be dealing with the experimental results and discussion.

2. Production Apparatus and Technique

In fig. 1 we show a schematic drawing of the production apparatus. It consists of a traditional vacuum plant including a rotary pump and an oil diffusion pump, with a liquid nitrogen trap able to reach an ultimate vacuum of about 10^{-6} torr in the experimental bell. The production plant consists essentially of two crucibles, C and E, filled by molten tin kept at two different temperatures T_1 and T_2 respectively. A niobium ribbon (some hundredths of millimeter of thickness) is passed at constant velocity through the tin bath by means of a suitable pulley mechanism.

The successive steps of the production process are the following. First we make a chemical etching of the niobium ribbon with a water solution of nitric and hydrofluoric acid in order to eliminate the surface impurities (mainly oxides) and to facilitate the diffusion of tin through the niobium surface. Then the ribbon is mounted in the vacuum system as it is sketched in fig. 1. After pre-heating by Joule effect in the length BC to a suitable temperature T_p the ribbon enters the crucible C where the first diffusion of

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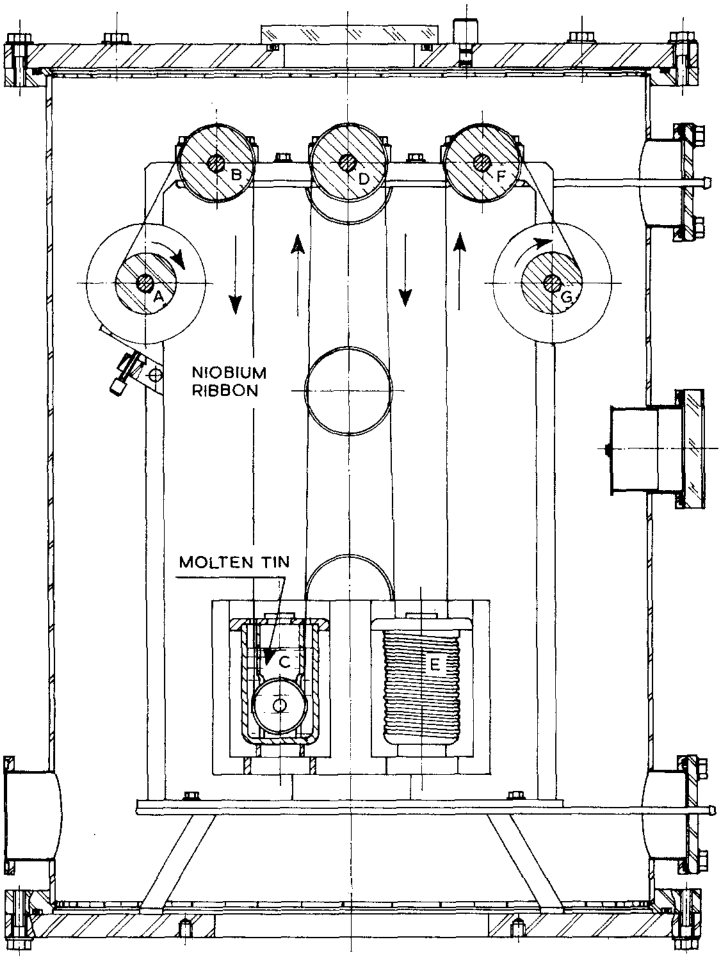

Figure 1 Schematic drawing of the production plant.

tin into niobium takes place. Next the ribbon comes out of the bath covered by tin, but the diffusion process continues because in the length CD the temperature T_D of the ribbon is kept quite high again by Joule heating. The subdivision of the diffusion process into two successive stages allows the reaction time to be increased without excessive contamination of the tin bath and, furthermore, gives the possibility of giving suitable thermal treatments on the ribbon. Because of the high temperature of the length CD that part of tin which does dot diffuse evaporates from the surface so that the ribbon reaches the point D almost free of tin. As it is very difficult to put the stabilising material directly on the Nb_3Sn layer it is necessary to give some preliminary treatment to the Nb_3Sn surface. In our case we dip the ribbon in molten tin in the crucible E whose temperature T_2 is high enough to obtain good tinning of the surface but, at same time, low enough to avoid any influence on the Nb_3Sn already formed.

The temperatures T_P and T_D are kept constant by means of stabilised current power supply and are controlled by an optical pyrometer with a precision of $\pm$ 5° C. The temperatures T_1 and T_2 are measured by Pt-PtRh 10% thermocouples with a precision of $\pm$ 5° C. The thermocouples also drive an electronic device which controls the current to the crucible heaters.

It is clear that, once we have fixed the velocity and the geometry of the apparatus, we have four parameters (T_1, T_2, T_P, T_D) which must be optimised in order to get a ribbon with reliable super-conducting properties.

3. Measuring Apparatus and Technique

The determination of the superconducting properties of our samples consists essentially in the measurement of the critical current I_c in a magnetic field, parallel to the ribbon plane and perpendicular to the direction of the current flowing through the sample. The magnetic field is generated by a superconducting solenoid with inner diameter of 4 cm able to reach a maximum field of 72 kG at 4.2° K. The samples, whose standard length is 3 cm, are mounted on a sample-holder (see fig. 2) which can be introduced into the helium bath and extracted from it without the necessity of disconnecting the magnet from the external power supply. Both the sample current leads and the magnet leads have been made by a special technique [9] in order to minimise the liquid helium consumption. Moreover a copper shunt whose resistance is about 1 mOhm, is placed in parallel with the sample for the purpose of stabilising the sample when it is superconducting and to prevent its destruction at the transition to the normal state.

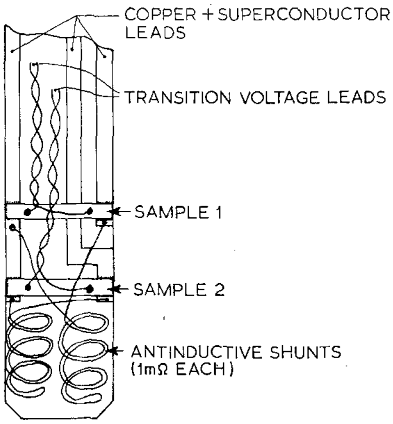

Figure 2 Schematic drawing of the sample holder.

The transition (see fig. 3) is detected by recording the voltage on the sample taken at two contacts 2 cm apart. We have defined, in analogy other workers the critical current I_c of the sample as the value of I corresponding to a measured voltage of 10 μV.

We point out also that the critical current is measured at a fixed magnetic field by increasing the current from zero to I_c.

4. Experimental Results and Discussion

The procedure by which we have found the values of T_P, T_1, T_D and T_2 corresponding to the best superconducting properties are the following:

(*a*) First we have kept fixed the temperatures T_1, T_D and T_2 at a value (~ 950° C) such that, according to the phase diagram of the Nb–Sn system (see fig. 4), we had formation of Nb_3Sn. Then we have varied T_P in the range from 850 to 1000° C. The critical current of the samples was quite independent of T_P and also quite low. Presumably this is due to an annealing of the

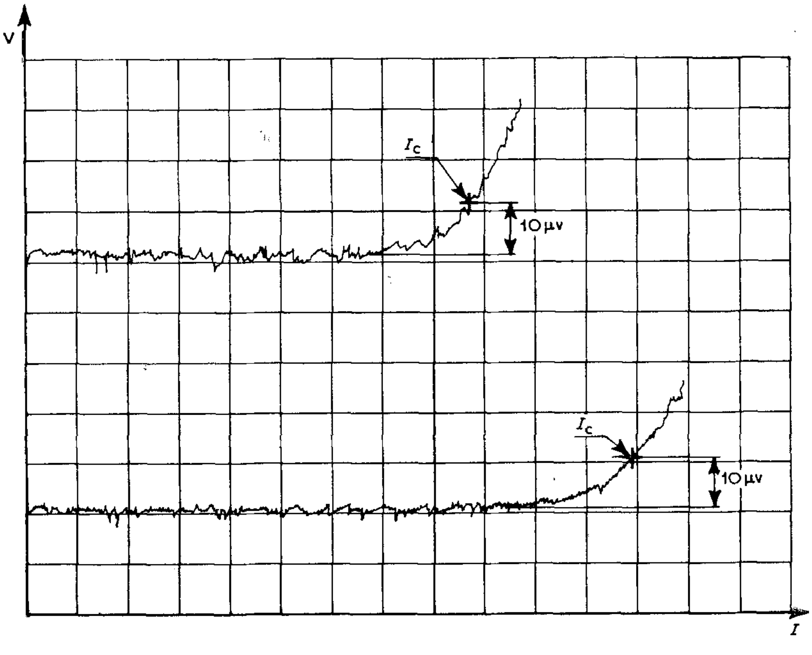

Figure 3 Typical *x–y* plotter graphs of transition curves.

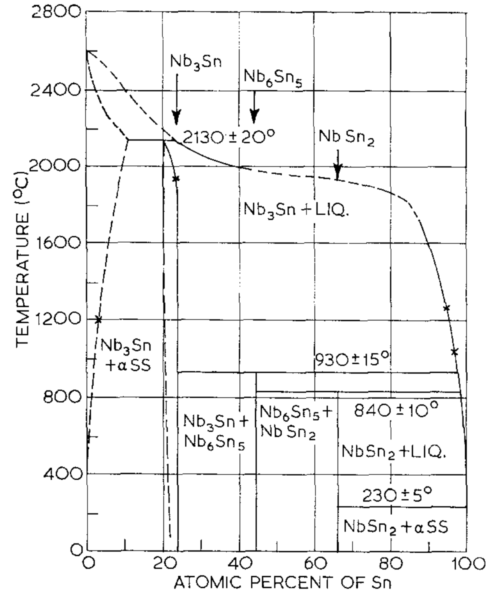

Figure 4 Phase-diagram of the Nb–Sn system (after reference [10]).

material at some stage of the production process, subsequent to the formation of Nb_3Sn. After that we have reduced T_2 to 400° C obtaining a general improvement of the superconducting properties and a maximum in the critical current in correspondence of $T_P = 950°$ C. The I_c vs. T_P plot is shown in fig. 5.

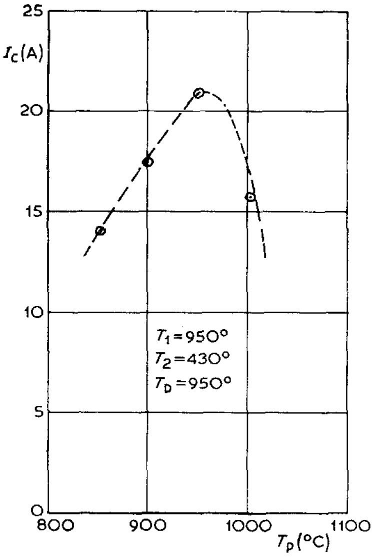

Figure 5 Behaviour of the Nb_3Sn critical current (measured at a field of 64 kG) as a function of T_p. Dimensions of ribbon: 2 × 0.03 mm; sliding velocity: 5 m/h; base material: Nb 99.9% partially annealed.

(*b*) The optimation of T_1 and a further confirmation of the validity of the chosen value of T_P have been obtained by producing a set of Nb_3Sn samples varying both T_1 and T_P from 900° C to 1000° C. In this case we have eliminated the diffusion in the length CD and the tinning process in the crucible E in order to substantiate better the possible correlation between T_1 and T_P. The experimental results concerning these samples are summarised in fig. 6. It is evident that the best superconducting properties correspond to both T_1 and T_P being about 950° C. We point out also that the values of I_c reported in fig. 7 are less than those reported in fig. 8 although the latter are measured in a higher magnetic field. This shows clearly the importance of the successive production stages which are absent in this case.

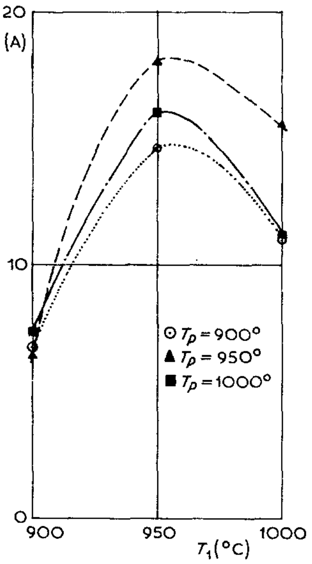

Figure 6 Behaviour of the Nb_3Sn critical current (measured at a field of 32 kG) as a function of T_1 for different values of T_p. Dimensions of ribbon: 2 × 0.1 mm; sliding velocity: 5 m/h; base material: Nb 99.9% partially annealed.

(*c*) In fig. 8 we have plotted the measured values of I_c as a function of T_2 and T_D taking fixed T_P and T_1 both at 950° C. It is quite evident that the higher values of I_c correspond to T_D and T_2 in the ranges 800 to 900° C and 400 to 700° C respectively. The best results so far obtained occur when $T_2 = 600°$ C and $T_D = 850$ to 900° C.

The results we have been dealing with until now are relative to samples which have been produced employing a niobium ribbon of nominal purity as follows: Fe 0.02 %, Ta 0.02 %,

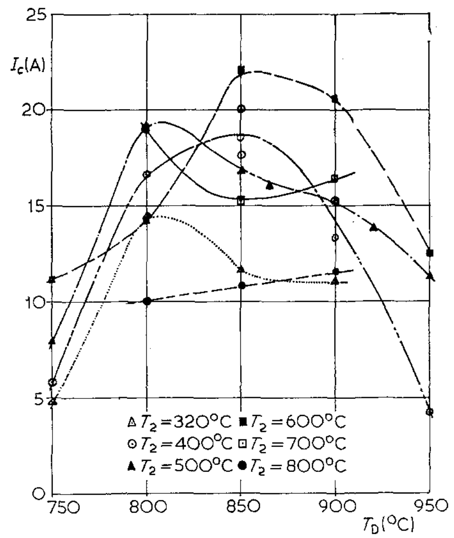

Figure 7 Behaviour of the Nb_3Sn critical current (measured at a field of 64 kG) as a function of T_D for different values of T_2. Dimensions of ribbon: 2 × 0.1 mm; sliding velocity: 5 m/h; base material: Nb 99% partially annealed.

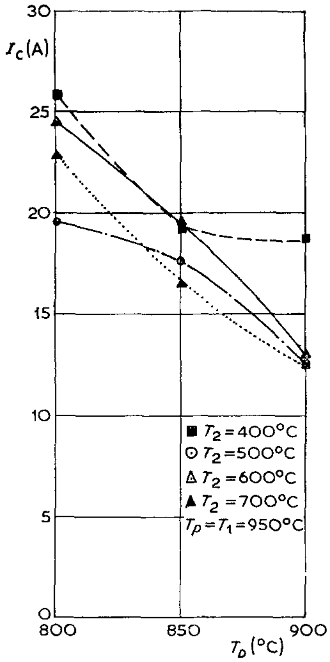

Figure 8 Behaviour of the Nb_3Sn critical current (measured at a field of 64 kG) as a function of T_D for different values of T_2. Dimensions of ribbon: 2 × 0.03 mm; sliding velocity: 5 m/h; base material: Nb 99.9% cold worked.

C 0.02% and other residuals (Ni, Mo, Si, Mg) 0.04%. Such a material is partially annealed. Recently we have used also a niobium ribbon of the same nominal purity but cold worked. Samples produced by using this material have critical currents 20% higher than those previously reported. Such preliminary results are shown in fig. 8. This increase of I_c could be due to an increased thickness of the Nb_3Sn layer on the cold-worked niobium substrate, although a previously mentioned work [5] seems to indicate that this is not the case.

We emphasise, however, that in a recent work on the constitution diagram of the niobium-tin system [8], the degree of cold-work has been shown to have an effect on the Nb_3Sn growth when niobium cans are used, while sheets samples are substantially unaffected. Furthermore in these papers the occurrence of irregular layers of Nb_3Sn is reported.

Because of this last problem we have not be able, up to date, to give a more significant information, i.e. a correlation between the changes of the experimental conditions and the corresponding changes of the critical current density.

Work is in progress to clarify this point, as well as to get experimental evidence of the suggested presence of more tin rich compounds which can act as pinning sites. We point out also that we have made some preliminary tests on samples obtained starting from a Nb–Zr 1% ribbon in view of the fact that the presence of a certain amount of zirconium can enhance the pinning efficiency [10]. However no effect of this kind has been noted as it can be seen from the plot of fig. 9. On the other hand we have not made a systematic study of the influence of zirconium varying its concentration in niobium and it may be that the optimum values of the various temperatures in this case are different from the previous ones. A deeper investigation about this argument will be part of our future research program.

Finally an investigation of the influence of the sliding velocity of the ribbon has been made by reducing the velocity by a factor three. Of course we have observed an increase of about 10% of I_c due to the higher thickness of Nb_3Sn layer formed but such an increase does not counterbalance the slowness with which the superconducting material is produced.

A qualitative discussion of our results can be carried out on the basis of the phase diagram reported in fig. 4 (after reference [11]). It can be seen that formation of Nb_3Sn takes place mainly at temperatures above 930°C, but, in the niobium-

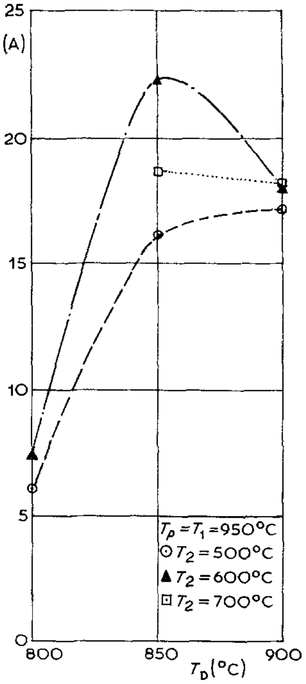

Figure 9 Behaviour of the Nb_3Sn critical current (measured at a field of 64 kG) as a function of T_D for different values of T_2. Dimensions of ribbon: 2 × 0.1 mm; sliding velocity: 5 m/h; base material: Nb–Zr 1%.

rich side, such a compound forms also at temperatures well below. However in this case there is simultaneous formation of other tin-rich compounds whose presence can be useful to a certain extent. The fact that the best superconducting properties correspond to the temperature values $T_1 = 950°$ and $T_D = 850°$ C or slightly less can be explained, on the basis of the phase diagram, in the following way. In the first crucible there is essentially formation of Nb_3Sn while in the processes which take place after completion of the diffusion, say after point D (see fig. 1), the temperature is such that the formation of tin-rich phases mainly Nb_3Sn with critical temperatures and fields considerably less than those of Nb_3Sn is possible. Such phases, mixed together with Nb_3Sn compound, are normal at 4.2° K and can act to a certain extent as pinning centres for the vortex lines so that their presence can contribute to the increase of the critical current I_c. Then the optimum value T_D 850° C can be due to a compromise between the amount of Nb_3Sn which forms and the number of pinning centres which are introduced in this way. On the other hand the optimum of T_2, falling in the range from 400 to 600° C, can be indicative of the fact that at higher temperatures the tinning process leads to an excessive formation of spurious phases while, at too low temperatures, the adhesion of tin to the ribbon surface is poor.

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