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G. Pasotti, M.V. Ricci, N. Sacchetti, G. Sacerdoti and M. Spadoni: Nb_3Sn DIFFUSION LAYERS. AN EXPERIMENTAL STUDY OF THEIR SUPERCONDUCTING PROPERTIES AS RELATED TO THE Zr CONTENT AND COLD WORK AMOUNT OF THE Nb BASE RIBBONS.

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Nb_3Sn DIFFUSION LAYERS. AN EXPERIMENTAL STUDY OF THEIR SUPERCONDUCTING PROPERTIES AS RELATED TO THE Zr CONTENT AND COLD WORK AMOUNT OF THE Nb BASE RIBBONS(*).

ABSTRACT. -

An extensive study of the superconducting properties of Nb_3Sn diffusion layer has been made in order to clarify the influence of cold work and the zirconium content of the niobium base ribbons on these properties.

Result concerning the critical current density, the critical temperature as well as the diffusion depth are reported and discussed.

The main points are that while the presence of some percentage of Zr is effective in increasing the critical current density J_c at the same time it causes a decrease in the diffusion depth. Good critical current values could be obtained by a compromise between these two opposite effects, reaching an increase of the critical current of 10-15%. More important is the effect of cold work on the base ribbons which results in a maximum increase of the critical current of about 30%.

(*) - Work partially supported by CNR.

INTRODUCTION. -

The noticeable superconducting properties of the A 15 compound Nb_3Sn were established several years ago. The most important techniques which have been developed to fabricate this compound in a conductor form are : vapour deposition(1) and diffusion of tin into niobium, in the liquid state(2) or, more recently, in the solid state(3) (bronze). By using the diffusion process one can try to control the amount of pinning centres in Nb_3Sn layers through appropriate cold working and alloying with other metals (e. g. Zirconium) of the Nb bas ribbons.

No systematic study of the combined influence of these two factors on the superconductivity properties of Nb_3Sn layers has been reported in the literature.

We have employed the diffusion technique to obtain Nb_3Sn layers on base ribbons whose Zr content ranged from 0% to 7% at. and cold work from 0% to 80%.

In the first section the main characteristics of the base ribbons are presented. In the second the diffusion process is described, while the third contains a description of the techniques used to measure the superconducting properties. Finally, in the fourth section, we present and discuss the experimental results.

1. - BASE RIBBONS. -

Ingots of Nb with different Zr content have been melted by an electron gun in a vacuum less than 10^{-6} torr at the beginning of the process and no higher than 5×10^{-5} torr at the end.

Wires of the required diameter have been obtained by means of a swaging machine.

For each percentage of Zr, by cold rolling and appropriate heat treatments, ribbons 0.1 mm thick, 4 mm wide with 0, 20, 40, 60, 80 %

of cold work have been prepared. Details of the fabrication process have been published elsewhere[4].

In Table I the chemical composition of the base ribbons is tabulated. No appreciable contamination of the material has been observed in the rolling process except a slight increase of the hydrogen, oxygen and nitrogen content.

TABLE I - Chemical composition of Nb-Zr base alloys.

Nominal composition	Zr %	Fe ppm	Co ppm	Ni ppm	Al ppm	Ti ppm	Pb ppm	Cr ppm	Mn ppm	H ppm	N ppm	O ppm
pure Nb	0	10	< 5	< 5	< 10	12	7	< 5	< 5	10	250	500
Nb-1% Zr	1.03 ± 006	10	< 5	7	< 10	5	6	< 5	< 5	10	150	250
Nb-2% Zr	2.3 ± 0.2	12	< 5	< 5	< 10	7	5	< 5	< 5	12	170	350
Nb-3% Zr	3.3 ± 0.3	12	< 5	< 5	< 10	7	5	< 5	< 5	12	130	230
Nb-5% Zr	5.4 ± 0.3	11	< 5	< 5	< 10	6	8	< 5	< 5	12	120	220
Nb-7% Zr	6.9 ± 0.7	10	< 5	< 5	< 10	5	9	< 5	< 5	11	150	180

2. - DIFFUSION PROCESS. -

The base ribbons are etched with an acid solution (HNO_3 7 %, HCl 20 %, distilled water 10 %), whased in pure alcohol, and then mounted in the apparatus shown in Fig. 1. Here the ribbon is pre-heated by the furnace P at a temperature T_P = 900 °C and then enters the crucible 1 that contains molten tin at a temperature T_1. The diffusion process continues in the furnace D at a temperature T_D. The second crucible 2, containing tin at a much lower temperature (400 °C), has been used sometimes to produce a layer of tin on the surface of the ribbon which makes soldering of a stabilisation tape easier. The velocity of the ribbon (5 m/h) has been chosen as a compromise between a long diffusion time and a short residence in the liquid bath since the molten tin is very corrosive at temperatures around 900 °C. The total diffusion time (crucible 1 and furnace D) is about 5 minutes.

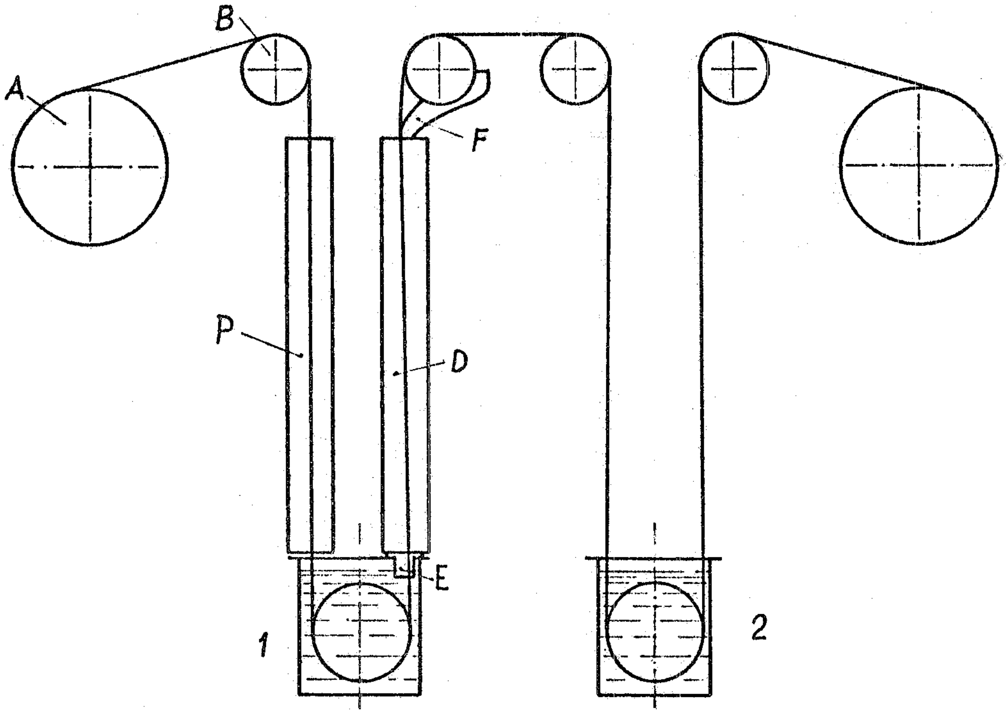


FIG. 1 - Schematic drawing of the Nb_3Sn diffusion apparatus.

The graphite cylinder E avoids a temperature dip between the molten tin surface and the furnace D. We have found that this is necessary because otherwise the superconducting properties of the Nb_3Sn get worse, due to the formation of tin-rich, non superconducting phases.

The "cold finger" F, which is water cooled to make the temperature of the ribbon drop rapidly to a low value, has the same purpose. The temperatures of the furnaces and of the crucibles, measured by chromel-alumel thermocouples, are kept constant within $\pm 5\,^{o}C$. The whole apparatus is contained in a vacuum chamber whose pressure is less than 10^{-5} torr.

3. - MEASUREMENT TECHNIQUES. -

The short sample critical current I_c of the diffused tapes has been measured at $4.2\,^{o}K$ in a superconducting magnet. The samples are mounted in such a way that the field is perpendicular to the current but parallel to the face of the ribbon. I_c is defined as the value of the curr ent that develops a voltage of 10 μVolt along the sample.

The critical temperatures T_c and the normal resistivities ρ_N have been measured in a variable temperature cryostat. A calibrated germanium resistance thermometer has been used.

The thickness d of the Nb_3Sn layers has been measured by a metallographic microscope after identification of the phases by a conventional anodizing technique.

4. - EXPERIMENTAL RESULTS AND DISCUSSION. -

4. 1. - Diffusion temperature effect.

The temperatures T_1 of the crucible and T_D of the diffusion furnace are critical for the formation of Nb_3Sn. Then optimization of their values has to be done before studying any other effect. Figures 2 and 3 show the effect of T_D on the critical current I_c. In Fig. 2 also the effect of T_1 is shown while in Fig. 3 also the effect of cold work is apparent. These data indicate that the highest values of I_c are always obtained when $T_1 = 950\,^{\circ}C$ and $T_D = 900\,^{\circ}C$. Fig. 4 shows that this optimum value of T_D is also independent of zirconium content. However it is interesting to observe how zirconium affects the shape of the curves. For a higher Zr content there is correspondingly sharper peak.

Measurements of the thickness d of the Nb_3Sn layer make possible the calculation of the critical current density J_c and the explanation of the maximum of I_c for a well defined value of T_D.

By increasing T_D the thickness d increases (Fig. 5) as :

$$\log d = A - \frac{B}{T_D} \qquad (1)$$

This is in good agreement with a diffusion equation[5] :

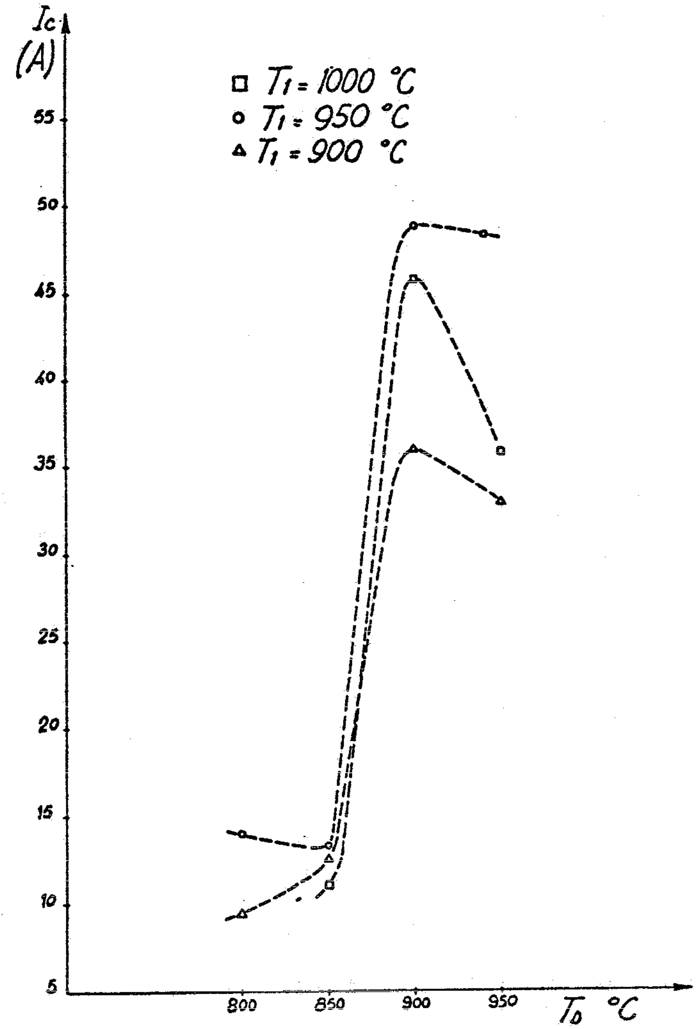


FIG. 2 - Critical current I_c v.s. T_D for different values of T_1. Data shown refer to Nb_3Sn grown on Nb-3%, Zr ribbons and similar results hold for other samples.

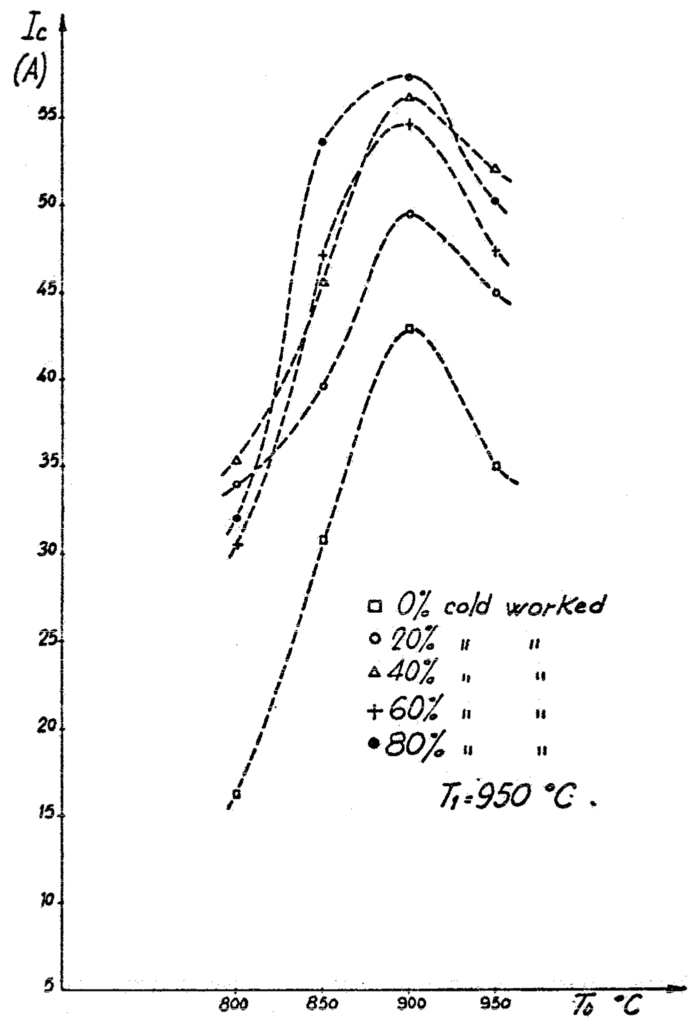
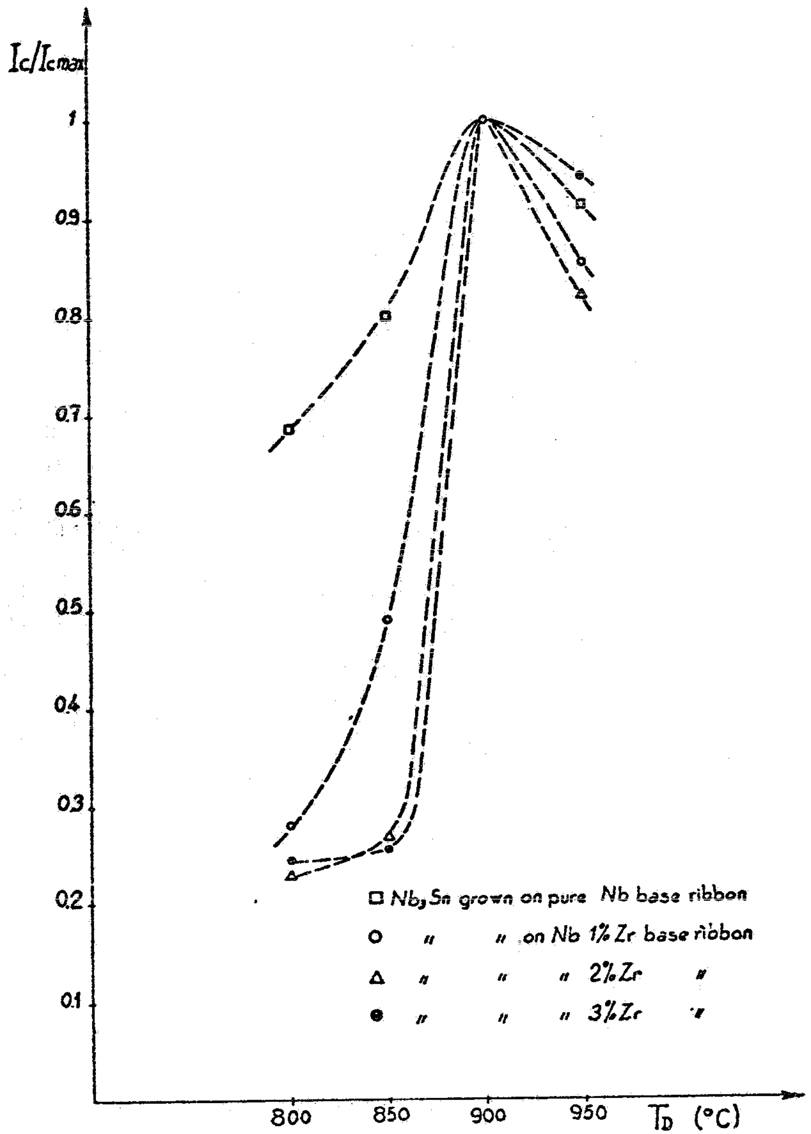


FIG. 3 - I_c v.s. T_D for different amount of cold work at fixed $T_1 = 950^oC$. Data shown refer to Nb_3Sn grown on pure Nb substrates and similar results hold for other samples.



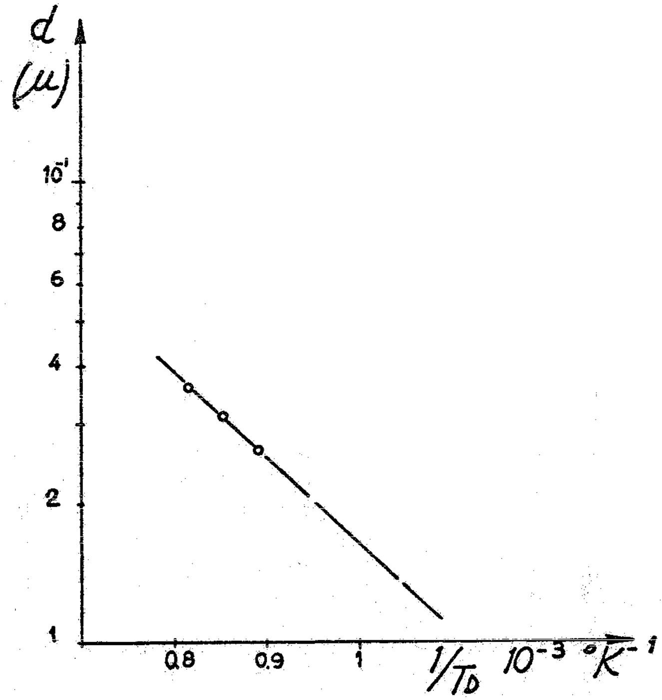


FIG. 5 - Diffusion thickness d as a function of $1/T_D$.

FIG. 4 - I_c as a function of T_D for Nb_3Sn grown on ribbons of different composition.

$$d^2 = 2 t D_o \exp(- \frac{Q}{R T_D}) \quad (2)$$

where Q is the activation energy and D_o the frequency factor and t the time. By comparing eq. (2) to the experimental results of Fig. 5, one obtains $Q = 18.6$ Kcal/mole and $D_o = 76 \times 10^{-8}$ cm^2/sec. Similar measurements by Old et al.[6] showed a quite different temperature dependence, but their data refer to a higher temperature range where a different mechanism of formation of Nb_3Sn (solution-deposition mechanism) is more efficient.

In Fig. 6 the critical current density J_c is plotted as a function of T_D. J_c always decreases when T_D is increased. Measurements of the normal resistivity ρ_N of the base ribbon before and after diffusion, show a reduction of ρ_N which is certainly due to a partial elimination of dislocations. The fact that J_c of Nb_3Sn decreases by increasing T_D,

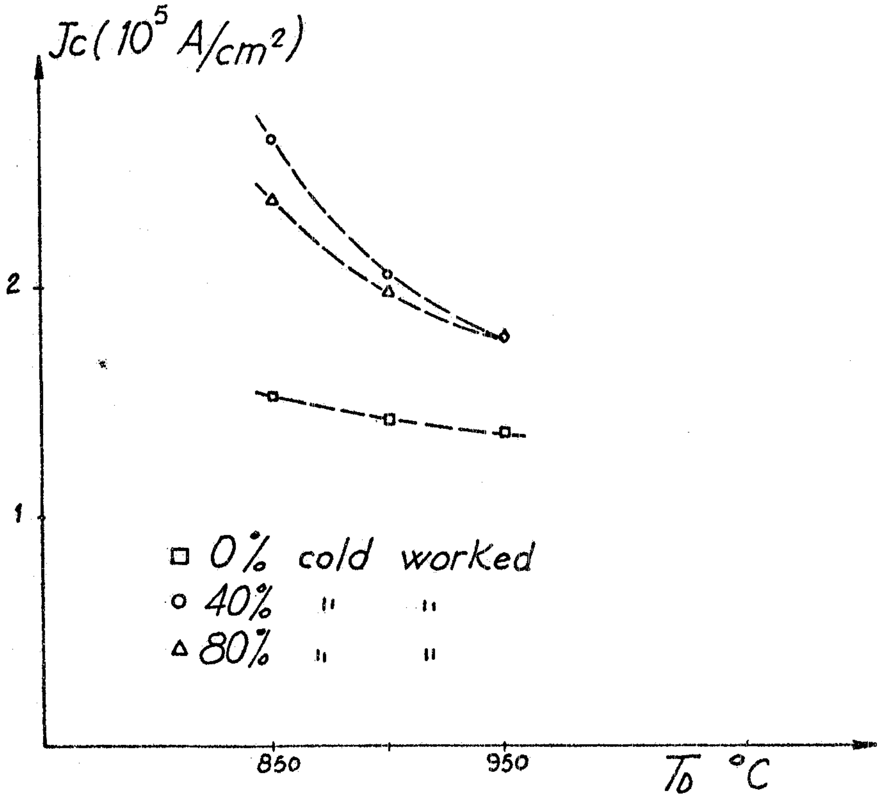


FIG. 6 - J_c v.s. T_D for Nb_3Sn grown on pure Nb substrates. Similar results hold for other samples.

indicates that the dislocations of the base ribbon could act as pinning centers in the diffused layer. We will discuss this conclusion in connection with the effect of cold work.

4. 2. - Effect of the Zr content of the base ribbon.

The influence of alloying with Zr on I_c and the diffused layer thickness d is shown in Figures 7 and 8. In Fig. 9 the critical current density is given as a function of the Zr content. These data clearly indicate that alloying the base ribbons with Zr has two opposite effects: J_c increases but the thickness d decreases. It is well known that the introduction of impurities increases the pinning efficiency. Considering this our results on J_c are as expected. The reduction of d is due to the influence of Zr on the parameters Q and D_o. We have found that the dependence (2) is still valid for ribbons doped with Zr, but the coefficients Q and D_o become : Q = 10.6 Kcal/mole, $D_o = 2.84 \times 10^{-8}$ cm^2/sec for Nb - 1% Zr; Q = 7.9 Kcal/mole, $D_o = 0.49 \times 10^{-8}$ cm^2/sec for Nb - 5% Zr. It is hard to explain this effect, mainly because the diffusion mechanism

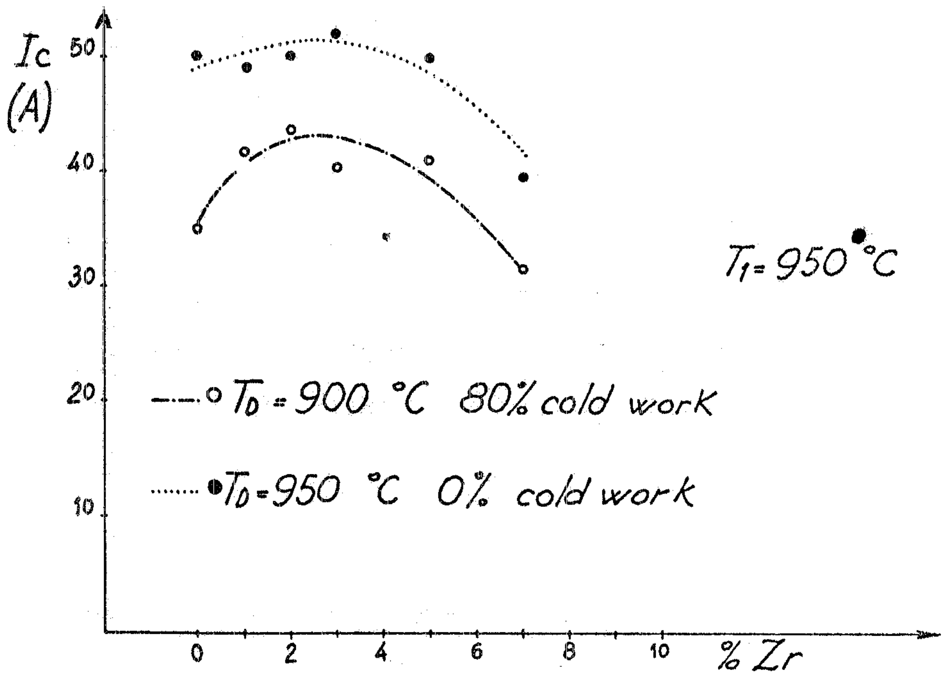


FIG. 7 - I_c v.s. zirconium content.

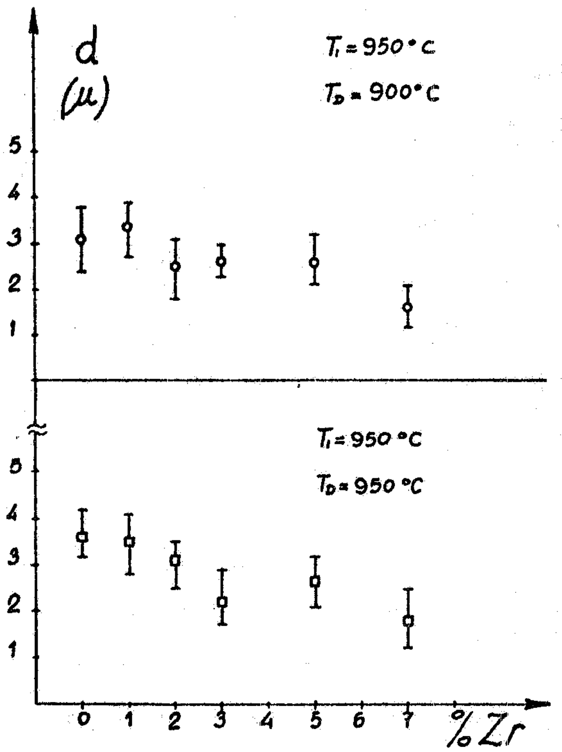


FIG. 8 - Diffusion thickness d as a function of zirconium content.

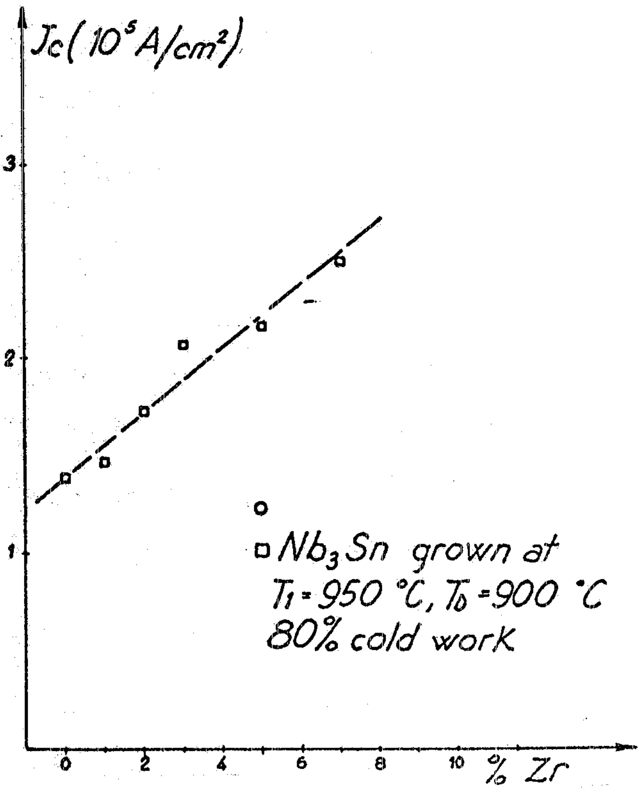


FIG. 9 - Critical current density J_c v.s. zirconium content.

is complicated by the fact that, at the same time, a chemical reaction takes place. The diffusion mechanism in poliphase systems has been studied by Kidson(7).

4.3. - Critical temperatures.

It has been found that the critical temperature T_c of the Nb_3Sn of our ribbons is independent of T_1 and cold work amount, but increases appreciably with T_D (Fig. 10) and weakly with Zr content (Fig. 11). The sharp decrease of T_c when T_D is lower than 900 °C is due to the formation of non superconducting phases or to a modification of the stoichiometry.

4.4. - Cold work.

The dependence of the critical current on the cold work amount of the base ribbon has been measured. Actually Fig. 3 shows that the critical current increases with cold work. Fig. 12 summarizes the effect of

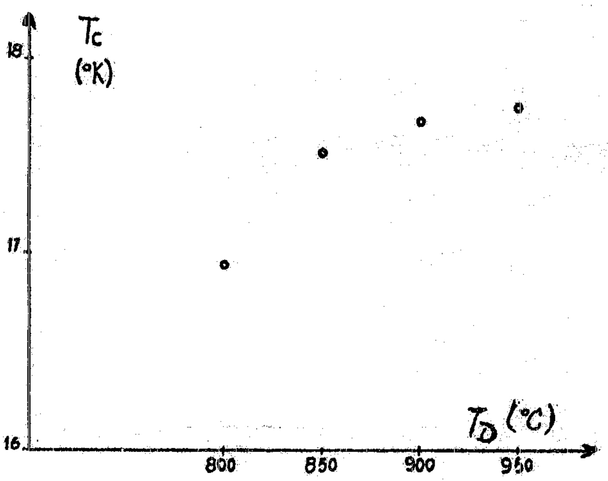


FIG. 10 - T_c of Nb_3Sn layers as a function of T_D.

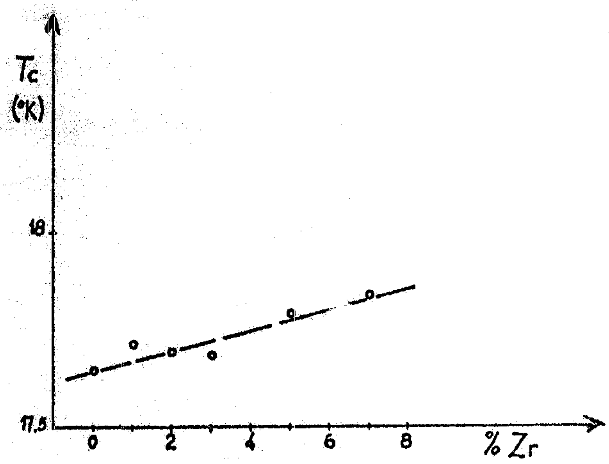


FIG. 11 - T_c of Nb_3Sn layers as a function of zirconium content.

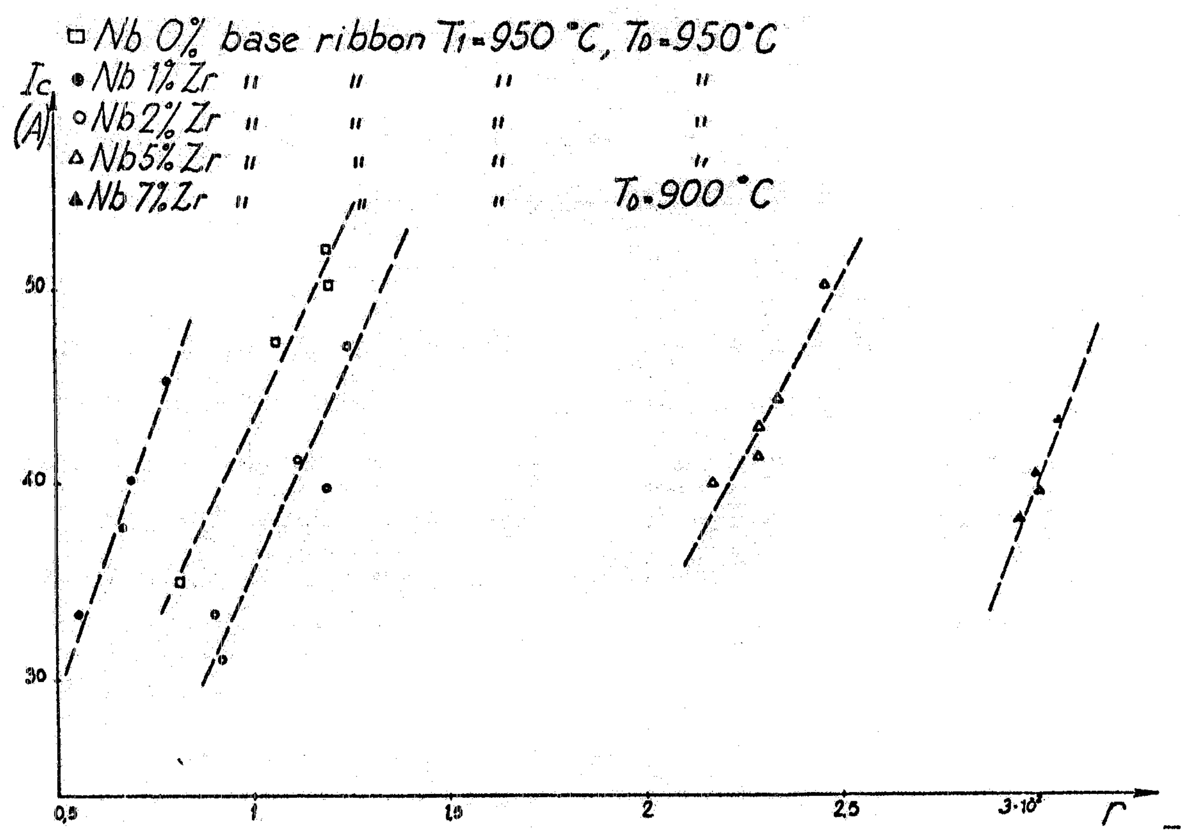


FIG. 12 - I_c v.s. residual resistivity ratio r for Nb_3Sn grown on ribbons of different zirconium content. Straight lines are least squares best fits of the experimental data.

cold work on the Nb_3Sn critical current. The residual resistivity ratio r, measured before diffusion, has been taken as a measure of the cold work amount. The diffusion process certainly reduces the number of dislocations and consequently alters r. However we have already seen, through measurements of r before and after diffusion, that this process causes a constant reduction of about 30 % on different samples. Fig. 12 shows that the increase of r by increasing the Zr amount is large, while, for each Zr content, the increase of r with cold work is small. This indicates that the residual resitivity is mainly determined by the Zr impurities. In spite of this, the effect of cold work on the critical current is much stronger than that of Zr. Since the thickness d has been found to be independent of cold work, the dependence of J_c on cold work is the same as that of I_c in Fig. 12. This shows that the pinning centres introduced by cold work are retained in the Nb_3Sn, and are more efficient than those introduced by Zr.

The anomalous behaviour of 0 % Zr samples, is probably due to the higher oxygen content of the base ribbon.

4.5. - Pinning.

For a better understanding of the pinning mechanisms acting in our samples, measurements of the critical current as a function of the applied field have been taken. Fig. 13 shows that the dependence of J_c on the field is the typical one of type II superconductors. This allows the utilisation of Coffey's theory[8] to evaluate Hc_2, the upper critical field. A value of 200 KG for all samples has been obtained. Fig. 14 shows that the normalized pinning force α / α_{max} (where $\alpha = J_c B$) plotted versus the reduced field $h = B/Hc_2$ has a maximum in the range $h = 0.17 - 0.23$.

The pronounced maxima of the pinning force fall at $h \simeq 0.2$ for all the samples, i.e. zirconium and cold work affect only the pinning force strength.

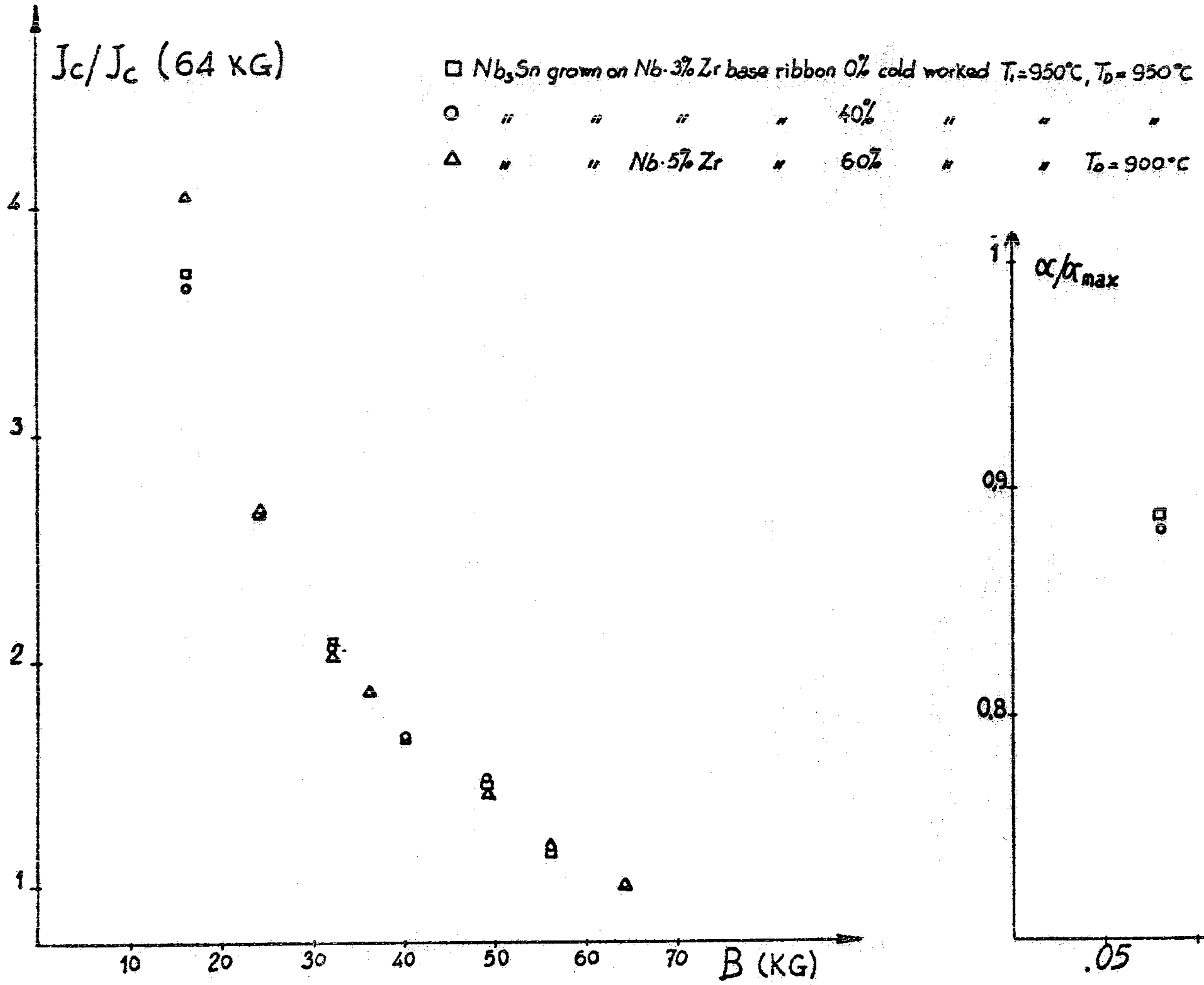


FIG. 13 - Plot of J_c/J_c(64 KG) v.s. applied field for some of our samples.

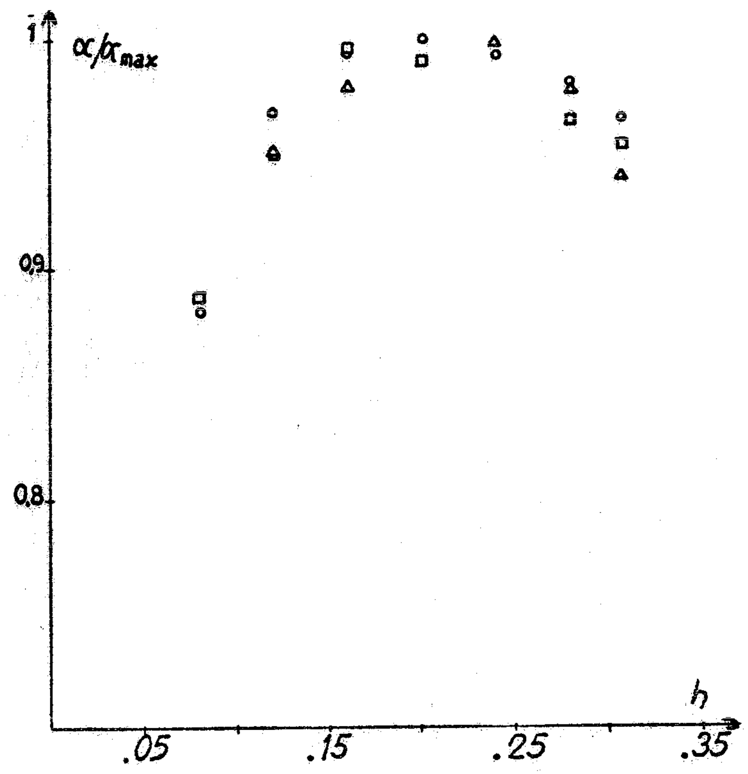


FIG. 14 - Normalized pinning force α/α_{max} as a function of the applied field for some of our samples.

Scanlan et al.[9] have observed pinning force maxima at $h \simeq 0.2$ for multifilamentary Nb_3Sn of small grain size, while tapes usually show maxima at $h \gtrsim 0.33$. They also quote that the pinning force maximum moves to lower values of h as the pinning force increases, i.e. as grain size decreases. Our results indicate that both cold work and zirconium content favour small grain size.

However we cannot exclude that zirconium and cold work could give rise to a different pinning mechanism superimposed to that caused by grain dimensions.

Suppose that the dense dislocation cell structure introduced on the base ribbons by cold work is partially retained in the Nb_3Sn structure; in such a case one can explain also the observed increase of pinning with Zr, probably due to a stabilisation of existing dislocations. This is a well known effect, the recrytallization temperature of many metals may be largerly increased when foreign atoms are soluted, even for low concentrations. It must be noted that Dew-Hughes[10] theory of flux pinning mechanisms in type II superconductors predicts that a dislocation cell-structure produce a maximum of the pinning force at $h = 0.17$, in good agreement with our hypothesis.

5. - CONCLUSIONS. -

The influence of Zr content and the amount of cold work on the properties of Nb_3Sn diffusion layers has been studied. The main points are that while the presence of some percentage of Zr increases J_c at the same time it causes a decrease in the diffusion depth. In order to achieve good current carrying properties a Zr content between 3 and 5 % is effective in increasing the initial current of 10 - 15 %. More noticeable influence comes from cold work amount. In fact increases of about 30 % in the critical current can be obtained in this way.

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