

The Mechanism and Kinetics of Growth of the Superconducting Compound Nb₃Sn

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A study has been made of the mechanism and kinetics of formation of Nb₃Sn from the elemental components. The Nb₃Sn forms partly by diffusion and partly by a solution/deposition mechanism which depends on thermal gradient mass transfer. The effect of this is to modify the growth equation to $x = kt^{0.36}$ over the temperature range 950 to 1150° C. The temperature dependence of these two processes, given by the difference between the activation energies for diffusion and solution, is -9.7 kcal/g atom (-0.42 eV/atom) so that the thickness of the Nb₃Sn layer produced in any given time decreases with increasing temperature.

Various experimental factors are discussed in terms of their influence on the rate of growth of the layer.

1. Introduction

During the last few years the compound Nb₃Sn has become increasingly important as a high-field superconductor because of its high critical field and critical temperature. Unfortunately from a technological point of view, these good physical properties are accompanied by extreme brittleness. The only way of obtaining practically useful conductors which can be bent round reasonably small radii and which make use of the good superconducting properties of Nb₃Sn is to produce them in a tape form containing a very thin layer of the compound close to the neutral axis. In this manner considerable flexibility can be retained without risk of damage to the superconducting layer.

In this connection, this paper presents a study of the formation of thin layers of Nb₃Sn by direct reaction between niobium and liquid tin.

2. Experimental Techniques

A series of preliminary sessile-drop experiments was carried out to see if the wetting processes had any effect on the subsequent reaction. Small pieces of tin weighing 0.5 g were placed on 0.125 in. thick × 0.5 in. diameter niobium discs in a tantalum resistance furnace and were heated to temperatures between 700 and 1200° C for periods of $\frac{1}{2}$ h to 8 h. A vacuum better than

5×10^{-5} torr was used up to 1100° C and an atmosphere of argon above this temperature.

The greater part of the work was concerned with the formation kinetics of Nb₃Sn and was carried out on niobium-tin diffusion couples made by drilling a piece of 0.2 in diameter tin rod and inserting a piece of 0.125 in diameter niobium rod in the hole. Both pieces of metal were ultrasonically cleaned in trichloroethylene before being sealed off in silica capsules under a vacuum better than 10^{-5} torr. The specimens were heat-treated in a horizontal resistance furnace for periods varying from a few minutes to 140 h.

For short time heat-treatments, e.g. 15 min, the time was considered to start when the furnace temperature returned to the original setting after the insertion of the specimen. The heating-up interval was 5 to 10 min, and must therefore be carefully considered when interpreting the structures observed in those specimens. Short-time experiments were also carried out using pressed niobium cups containing tin pellets in a high-frequency induction furnace. This technique provided sufficiently fast heating and cooling rates for realistic diffusion times of the order of one minute to be achieved.

After heat-treatment the couples were sectioned and polished using metallographic techniques developed in this laboratory for the

preparation of niobium alloys [1]. The phases were distinguished by anodising in 10% citric acid at 22.5 V [2].

The equilibrium diagram on which this study is based was determined in this laboratory [3].

Throughout the work, the materials used were spectroscopically pure tin supplied by Johnson Matthey & Co, and a commercial grade of niobium, the analysis of which is given at the end of this paper.

3. Experimental Results

Examination of the drop-substrate interfaces after reaction did not show any irregular effects and it was concluded that the wetting processes presented no obstacle to the subsequent diffusion.

Different substrate surface preparations were used, namely, as ground, as polished, and as polished and anodised. No effect was observed on the rate of spreading or drop profile.

The growth kinetics of Nb_3Sn in the range 950° to 1200° C were investigated using the diffusion couples. During the metallographic examination of the specimens it was noticed that the growth of the Nb_3Sn varied around the circumference of the rod, having in places a broken and crystalline appearance at the Nb_3Sn /tin interface. Fig. 1 shows a layer of Nb_3Sn of

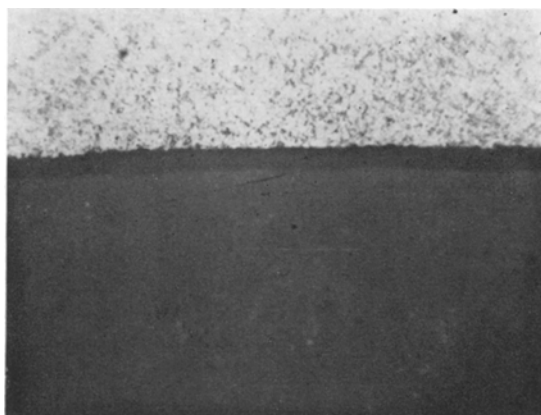


Figure 1 Smooth layer of Nb_3Sn formed after 4 h at 950° C ($\times 610$).

uniform thickness while on another area of the same rod, a rough layer such as that shown in fig. 2 was found. In general, the region of uniform thickness extended around the part of the circumference adjacent to the silica capsule. The

layer on the remaining two-thirds or so of the circumference was rough. Because of the variation in thickness of the Nb_3Sn , it was not possible to follow the rate of formation by measuring the width of the layer in the normal manner. The anodising technique was therefore slightly modified to give a colour range which could be differentiated by a Metals Research "Quantitative Television Microscope". This instrument was used to measure the area of the Nb_3Sn layer at eight equally-spaced points around the circumference and an average thickness of the Nb_3Sn was calculated.

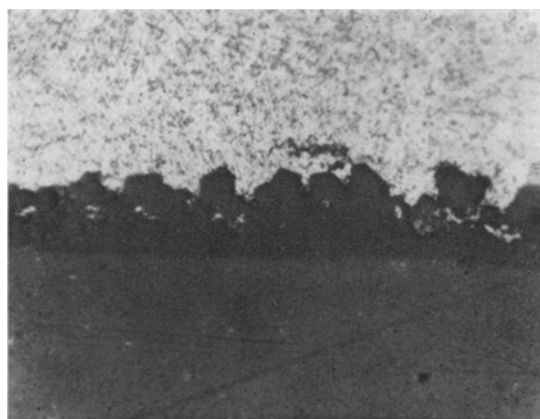


Figure 2 Irregular layer of Nb_3Sn formed after 4 h at 950° C ($\times 610$).

It is considered that the variation in growth of the Nb_3Sn is due to a solution/deposition mechanism. The experimental method used will inevitably lead to thermal gradients within the capsule. Since the solubility of niobium in tin increases with temperature [4], the layer will be dissolved in the hot regions of the couple near the capsule wall where it lies on the furnace floor and the niobium will be deposited as Nb_3Sn in the cooler regions. There will thus be thermal gradient mass transfer of niobium leading to an increased thickness of the layer in the cooler parts of the diffusion couple. Fig. 3 is a scanning electron microscope photograph of the surface of the Nb_3Sn after the overlying tin layer has been etched off. The surface of the Nb_3Sn is seen to be crystalline in form, many of the crystals showing a large, well developed form which is characteristic of growth from the liquid. Further evidence of this mechanism is provided by the presence of small crystals of $NbSn_2$ in the tin

after solidification. Since NbSn_2 is not stable above 850°C [3], these must have been precipitated on cooling, confirming the presence of an appreciable solubility of niobium in the tin at 950°C .



Figure 3 Scanning electron micrograph of Nb_3Sn crystals ($\times 2180$).

If the growth of the Nb_3Sn is controlled by diffusion then the thickness of the layer should follow a \sqrt{t} law, i.e.

$$x = kt^{0.5} \quad (1)$$

where x is the layer thickness after a time t and k is a constant. Straight lines of the form

$$\log x = m \log t + c \quad (2)$$

were therefore fitted to the data by the method of least squares and table I shows the slopes and the intercepts at one hour for each temperature. The slope remains fairly constant at 0.34 to 0.39 over the range 950° to 1150°C . The results at 1200°C do not fit this pattern, presumably because of the large amount of Nb_3Sn deposited in the liquid tin at this temperature. Hence, from equation 2 the growth of the Nb_3Sn layer between 950° and 1150° may be written

$$x = c' t^{0.36} \quad (3)$$

where c' is a constant given by $\text{antilog } c$ for any particular temperature and 0.36 is the average slope over the temperature range.

The index 0.36 in equation 3 indicates that the layer growth is slower than might be expected if the process were diffusion controlled (cf. equation 1). The constants in these two equations, k and

c' , are the rate constants for the processes involved and contain the temperature dependence of the reaction rate.

TABLE I

Growth kinetics of Nb_3Sn		
Temp ($^\circ\text{C}$)	Slope (m)	Thickness after 1 h (μm)
950	0.39	10.8
1000	0.35	9.7
1050	0.37	8.15
1100	0.34	7.6
1150	0.37	6.1
1200	0.23	7.0

4. Discussion

The effect of the solution/deposition mechanism on the growth kinetics of the Nb_3Sn has been taken into account by considering a model system in which the solution and deposition regions are equal in area.

The rate of growth of the layer is given by

$$\frac{dx}{dt} = \frac{k_1}{x} - k_2 \quad (4)$$

for the region where solution is taking place and

$$\frac{dx}{dt} = \frac{k_1}{x} + k_2 \quad (5)$$

for the deposition region. k_1 describes the growth of the layer by diffusion, and k_2 describes the effect of the solution/deposition mechanism. It is reasonable to assume that k_2 is independent of x , but an approximation is being made in assuming that it is independent of t for all values of t . The solution rate will not become constant until a sufficient time has elapsed for the liquid tin to become saturated with niobium; however, for the purposes of the present treatment, this time has been neglected.

Integration and combination of equations 4 and 5 lead to an expression for t in terms of a polynomial function of \bar{x} , the average thickness, i.e.

$$t = \frac{\bar{x}^2}{k_1} \left[\frac{5}{9} - \frac{28}{81} \frac{k_2 \bar{x}}{k_1} + \frac{34}{81} \frac{k_2^2 \bar{x}^2}{k_1^2} \dots \dots \right].$$

Thus the effect of the solution/deposition mechanism has replaced the term x^2 in the usual diffusion equation $x^2 = 2Dt$ by a polynomial series. The index 0.36 in equation 3 is an experimental approximation to the series obtained by expressing x as a function of t .

From equation 4 it is inferred that there is a

maximum thickness of the solution region which will be reached when the diffusion growth is counterbalanced by solution.

$$\text{Then } x_{\max} = \frac{k_1}{k_2}.$$

From the experimental data, a reasonable estimate of x_{\max} at 950° C is 25 μm , i.e. $k_1/k_2 = 2.5 \times 10^{-3}$ cm. Combining this value with the experimental results at 950° C, k_1 , the diffusion coefficient is evaluated as $\sim 10^{-10}$ cm²/sec.

A value of the observed resultant activation energy may be obtained from the slope of a graph of the rate of the process against $1/T^\circ \text{K}$ (fig. 4). If the layer thickness at 1 h is used as a measure of the rate of the process then the apparent activation energy is calculated to be -9.7 kcal/g atom. The negative value of the temperature dependence is an expression of the fact that as the temperature increases the solution part of the process increases more rapidly than the diffusion growth part, thus for any given time the average layer thickness decreases with rising temperature.

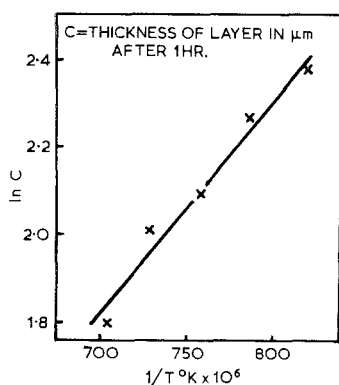


Figure 4 Temperature dependence of the growth rate of Nb₃Sn.

5. Factors affecting the growth of Nb₃Sn

5.1. Temperature Gradients

The results of these experiments show clearly that a considerable amount of the Nb₃Sn which forms does so by deposition from the liquid phase. The crystals then agglomerate and are slowly bonded together by the diffusion of niobium into the intermingling tin and its subsequent conversion to Nb₃Sn. It is not clear whether the niobium is transferred through the liquid tin by diffusion or by convection currents. A magnetic field of 3 kOe was applied during one

diffusion anneal in an attempt to damp out any convection currents in the liquid tin, but no difference was found in the mode of growth of the Nb₃Sn. It has been calculated that the required temperature gradient to account for the necessary difference in thickness is about 10° at 950° C assuming that the transfer depends entirely on diffusion. This difference is larger than might have been expected in the small silica capsule inside the furnace.

If, however, the problem is considered in terms of diffusion through a static boundary layer of liquid followed by convective transfer, then the diffusion distance is much reduced since typical thicknesses of boundary layers vary from 10⁻¹ cm to 10⁻³ cm. The mass flow may therefore be maintained by a much smaller concentration difference and hence the necessary temperature gradient is also reduced. For example for a static layer, 10⁻² cm thick, the temperature difference is reduced to < 1° C.

The convective flow velocity required to transport the dissolved niobium is calculated to be of the order of 10⁻³ cm/sec. This low velocity explains the absence of any effect due to the magnetic field.

It is seen, therefore, that the solution/deposition mechanism requires very small driving forces, and will be difficult to eliminate in practice.

5.2. Amount and Composition of Liquid Tin

The saturation of the tin with niobium before reaction would have little effect, since it would allow the transport of the niobium to begin immediately without a preliminary delay while saturation was reached.

The volume of the tin is important because this influences the amount of niobium which can be held in solution. Temperature gradients will also be minimised in an experimental configuration which is physically small in size, thus helping to restrict the mass-transfer mechanism.

5.3. Surface Condition of the Niobium

It was concluded from the experiments on wetting that the surface preparation of the niobium was not important, but it has been found that the presence of a thickened oxide film has an effect upon the growth of the Nb₃Sn. Where the compound layer is smooth, the oxide film can frequently be seen adhering very close to the surface. When the niobium was heated in air for 24 h at 200° C before reaction, the

subsequent growth of the Nb_3Sn was found to be dependent on the adhesion of the film. Fig. 5 shows that when the film breaks away, the growth is irregular. The position of the film is clearly marked by decoration with $NbSn_2$ crystals during cooling. The transition region demonstrates very clearly that a considerable amount of the niobium is consumed by solution in the tin.

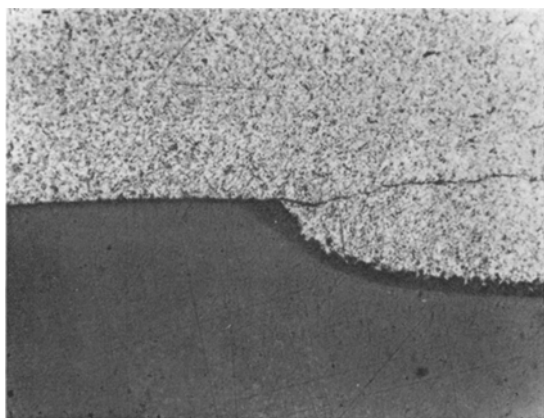


Figure 5 Transition region between adhesion and non-adhesion of a surface oxide film ($\times 610$).

5.4. Heating Rates

The heating rates used for the diffusion couples are slow enough to allow the formation of appreciable amounts of $NbSn_2$ before the diffusion temperature is reached. After short diffusion times some $NbSn_2$ is still present together with the Nb_3Sn . The subsequent transformation of the $NbSn_2$ to Nb_3Sn takes place in an irregular manner. In addition, some of the $NbSn_2$ also dissolves into the tin as the niobium solubility increases with increasing temperature. These two processes result in an irregular Nb_3Sn /tin interface. Observations have shown that the formation of Nb_3Sn is accomplished primarily by diffusion of the tin through the Nb_3Sn into the niobium. Consequently any cracks or fissures in the Nb_3Sn /tin interface cause indentations in the niobium/ Nb_3Sn interface and defects in the Nb_3Sn layer do not close up. A faster heating rate would largely preclude the formation of $NbSn_2$ and would give a more uniform layer of Nb_3Sn . Similarly a rapid cooling rate is also desirable, particularly if any excess tin is present

since this will react with the Nb_3Sn which has formed to give a decomposition product of $NbSn_2$.

5.5. Purity of Niobium

Niobium samples from different sources with purities varying from ordinary commercial grades to super-pure vacuum-annealed material were used in selected duplicate experiments to see if composition had any effect on formation of the Nb_3Sn . No significant differences were observed.

6. Conclusions

- (1) The growth of Nb_3Sn by direct reaction between niobium and liquid tin is a complex reaction involving both diffusion and a solution/deposition mechanism. The result of these two opposing processes has a negative temperature dependence which can be described by an apparent activation energy of -9.7 kcal/g atom. The detailed behaviour of the formation kinetics depends in practice upon the experimental configuration.
- (2) The chemical diffusion coefficient for the formation of Nb_3Sn is $\sim 10^{-10}$ cm²/sec at 950°C.
- (3) Because of the solution/deposition mechanism the volume of tin present is important. A minimum amount of tin leads to improved uniformity of the Nb_3Sn layers.
- (4) Rapid heating rates are desirable to prevent the formation of $NbSn_2$ which subsequently transforms to an irregular Nb_3Sn layer.
- (5) Growth of the Nb_3Sn layer occurs primarily at the niobium/ Nb_3Sn interface, suggesting that tin diffuses more rapidly than niobium through the Nb_3Sn layer.

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Appendix

TABLE I Niobium analysis

Impurities in ppm

O		H		N		C								
500		40		150		100								
Si	Ta	Fe	Mo	Ti	V	Cr	Mn	Co	Ni	Al	Mg	Pb	Cu	Sn
70	100	< 20	< 15	< 15	< 15	< 15	< 2	< 15	< 5	< 50	< 15	< 3	< 15	< 2