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Parameters affecting critical currents in superconducting Nb_3Al

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A.c. susceptibility measurements made on samples of Nb_3Al have shown that, even after extensive heat-treatments, significant amounts of degraded A15 phases are present. This low critical field material, resulting from vacancies on the niobium chains, limits the current carrying capacity of the bulk sample. The indication is that under favourable conditions the critical current density of Nb_3Al could equal or be superior to that of Nb_3Sn.

1. Introduction

For commercial applications the most important parameters of a superconductor are the critical current density and upper critical field. In solid solutions such as NbTi the factors determining these parameters are reasonably well understood. The critical current density is determined by the precipitates, or dislocations which provide pinning, while H_{c2} is determined by the mean free path. However, with intermetallic compounds such as Nb_3Sn and Nb_3Al, which can have the highest critical fields and current densities, the situation is much more confused. In general the longer the mean free path the higher is H_{c2} and the fewer phases present the higher the critical current density. This can be understood qualitatively in that H_{c2}, and hence J_c, are very dependent on the degree of order in the material; but the type of ordering, and what determines it, are still obscure. The object of this work was to try to obtain a better understanding of the factors which determine the critical current density in A 15 compounds, in particular in Nb_3Al.

2. Materials preparation

Most experiments were carried out on Nb_3Al. It is difficult to make satisfactory specimens since the A15 compounds form by a peritectic reaction and the aluminium has a high vapour pressure. Thus at any temperature which makes the aluminium sufficiently mobile to homogenize the material there will be problems with loss of aluminium from the surface.

Specimens were made by melting 99.95% pure Nb and 5N aluminium in an argon arc furnace. Aluminium losses were fairly small and consistent, so that where a particular composition was required allowances could be made. Analysis of the final ingot was made using an atomic absorption spectrophotometer. Other workers have made Nb_3Al [1, 3] by sintering powders but it was felt that material prepared from the melt would be more easily interpreted from the phase diagram.

The ingots were homogenized at 1500°C in a vacuum of 10^{-5} Torr for 24 h. They were then ordered at 750°C. This is the optimum ordering temperature according to Sahm and Pruss [4]. Weight losses were undetectable after these treatments.

The phases present in each sample were identified by X-ray powder diffraction patterns. The lowest concentration of a second phase which could be detected was about 10% and within this limit there was good agreement with the phase diagram suggested by Lundin and Yamomoto [5].

Although it was not difficult to produce single phase specimens with the A15 structure, most specimens still showed a dendritic structure. Fig. 1 shows such a structure. The material is 23 at.% Al, after homogenization for 24 h at 1500°C. Subsequent ordering at 750°C made no difference to the microstructure.

Unless otherwise stated, heat-treatments were carried out on ingots about 1 cm diameter, and 1 mm specimens were spark machined from these ingots.

3. Measurements

The majority of the data was obtained by

Figure 1 Nb_3Al, containing 23 at. % Al, showing the dendritic structure, × 80.

making measurements of the a.c. susceptibility when a small ripple was imposed on the main d.c. field. The details have been described elsewhere [6, 7] so only the main points will be summarized here. A coil is wound round the specimen and a compensating coil used to balance out the signal obtained at zero external field. The external field is raised and the signal plotted as a function of the amplitude of the a.c. ripple field. The signal is measured with a phase sensitive detector with a wide bandwidth so that the whole waveform is measured. The signal on the phase sensitive detector is then the average, over one period, of the voltage and hence proportional to the difference in flux in the specimen at the maxima and minima of the ripple field. This gives a good deal of information about the way flux is entering the sample.

If a model, such as the Bean model, is used to interpret the results the parameters of the model can be determined. However, there are some conclusions which are independent of the model. The first is the displacement of flux lines at the specimen surface. If these move a distance y the flux entering the specimen, ϕ, is related to this by $\phi = 2\pi a B_0 y$, where B_0 is the external flux density and a the radius. The second is the penetration of the signal. If the signal penetrates a distance x when the amplitude of the ripple is b_0 the flux is $b_0 x$. Thus a measurement of the flux gives a measure of the penetration of the signal. The interpretation of the penetration depends on the model used, i.e. whether an exponential decay, a linear decay as predicted by the Bean model, or some combination of the two. However, even without such models the qualitative conclusion can be drawn that only material within about x of the surface is affected by the ripple field.

If we assume that the current density is a function of the radius only, at a given external field, we can plot the pinning force at various radii and thus show up inhomogeneities on a macroscopic scale. This assumes the Bean model in its most general form, and it predicts a signal initially proportional to the square of the amplitude.

In practice the initial response is always linear, corresponding to the immediate penetration of small signals to a finite distance called the pinning penetration depth. This is a parameter independent of the critical current, but still in general determined by the pinning. In most materials measured previously it is between about 1 and 10 μm, and it can be explained by the assumption that flux lines are oscillating between, or within, their potential wells.

If the amplitude is increased beyond the linear region flux lines become unpinned and there is a gradual transition to the Bean model. The signals from the phase sensitive detector can be used to measure the force required to move the flux lines as a function of their displacement. It saturates at BJ_c per unit volume for very large displacements, thus allowing the calculation of the critical current density.

4. Results

4.1. A.c. measurements

The results were of two types. Firstly those of similar character to those found in Pb–Bi and other alloys, which could be interpreted using the models described above. Fig. 2 shows a number of graphs of the force on the flux lines against their displacement for those samples.

The second type occurred in samples measured at high fields, high temperatures, or those degraded by aluminium loss. These specimens had large linear signals and the force did not tend to a constant value which could be accurately associated with the critical current density. Some results of this type are shown in Fig. 3.

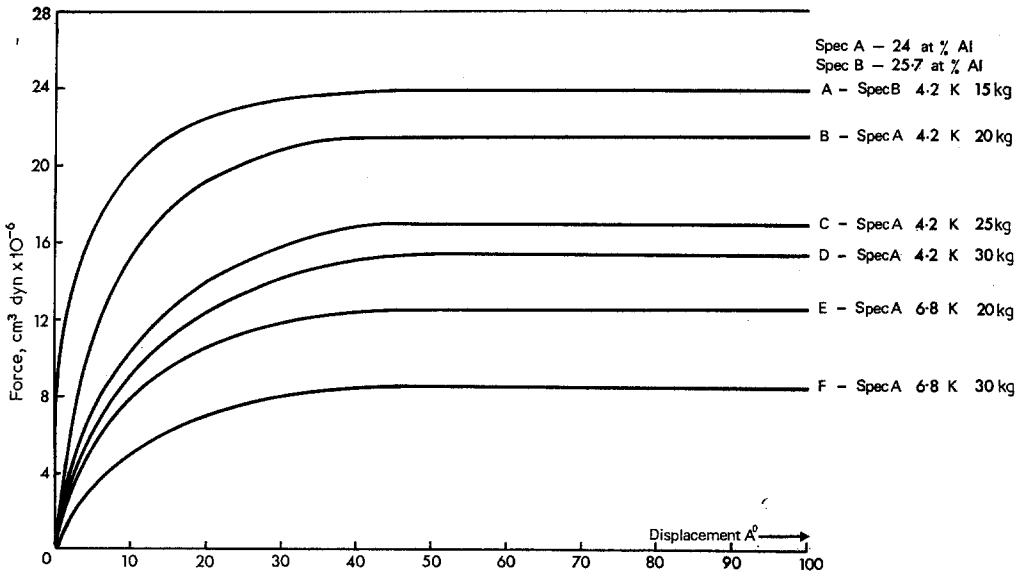

Figure 2 The pinning force as a function of flux displacement at low fields and temperatures.

4.2. Critical temperatures

Measurements of the critical temperatures of a wide range of alloys were made using the mutual inductance technique. Temperatures were measured with a gold iron/chromel thermocouple.

Powdered samples were used because they allow measurements to be made of the proportion of the sample with any given value of T_c, provided that the size of the powder is smaller than any inhomogeneities so that shielding effects do not occur. Typical particle sizes were about 5 μm. At any temperature the signal is directly proportional to the volume of normal material. It was found that the strain introduced by the powdering process broadened the transition but annealing at 750°C removed these effects. Fig. 4 shows four transition curves taken at various stages of an anneal at 750°C.

The results for all specimens examined are

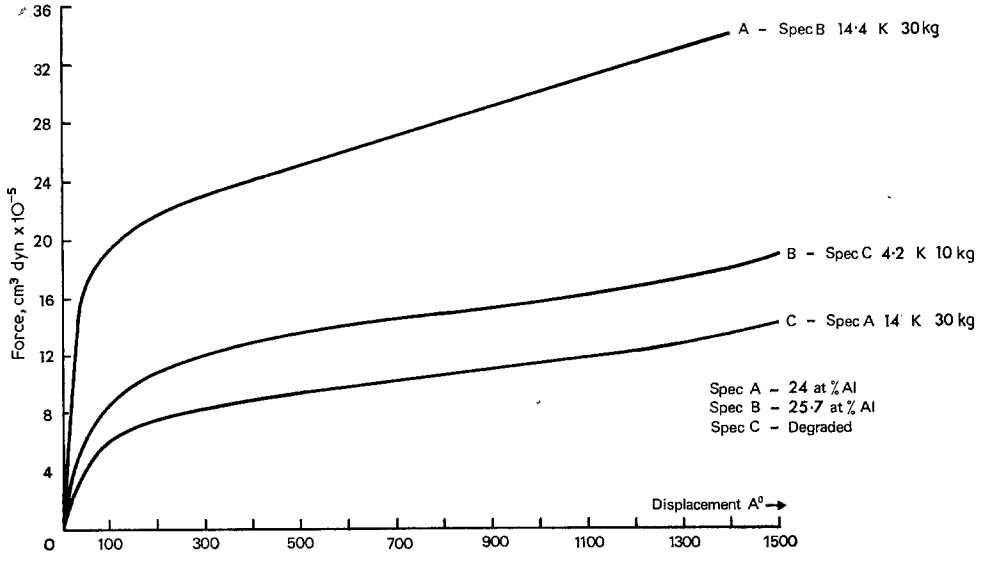

Figure 3 The pinning force as a function of flux displacement at high fields and temperatures.

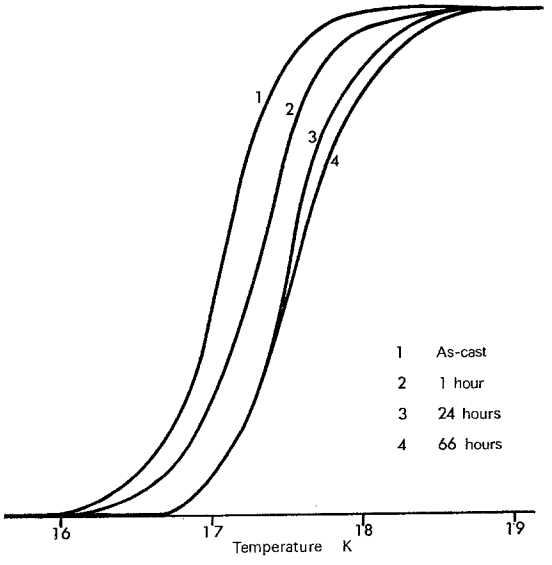

Figure 4 The effect of low temperature annealing on T_c.

shown in Fig. 5, where T_c is plotted against the overall composition of the sample. In the two-phase regions two transitions were observed corresponding to solid solution and A15 compound, and both are shown.

The superconducting materials fall into three groups. Firstly, the solid solution whose critical temperature is not very dependent on composition. The main points of interest lie in the A15 phase field. At the niobium-rich end there were still two transitions observable although the material was all A15. Fig. 6 shows an extreme sample made by over annealing so that a significant amount of aluminium was lost Even in this specimen no trace of solid solution could be detected. The most interesting question is to what extent double transitions are explained by a lack of homogeneity in the composition. An electron probe microanalysis showed composition variations of less than 2% of Al content. Since the range of the double transitions is greater than this it follows that over at least some of the composition range two forms of Nb_3Al exist at the same composition with different critical temperatures. This will be discussed further below.

On the aluminium-rich side of the phase diagram the transitions were found to be broader as indicated by the dotted line showing the continuous range of T_c at these compositions. No alloy containing only Nb_2Al was superconducting and no two phase alloy containing it showed a second transition. We conclude that Nb_2Al is not superconducting.

4.3. T_c measurements in high fields

Provided that shielding effects are small, the size of the signal in a measurement of T_c shows how much of the sample is normal at any temperature. Thus if we plot the signal as a function of

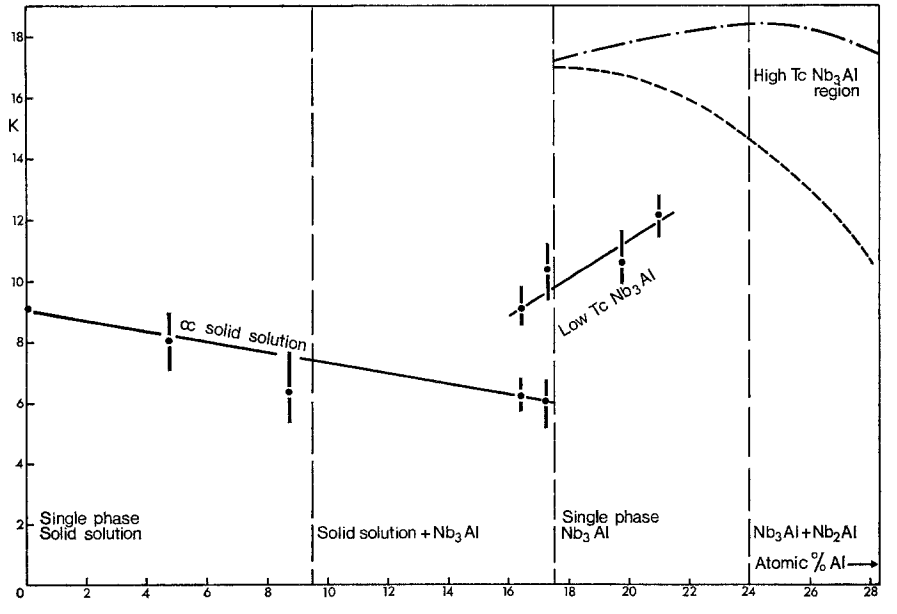

Figure 5 The variation of T_c with overall composition.

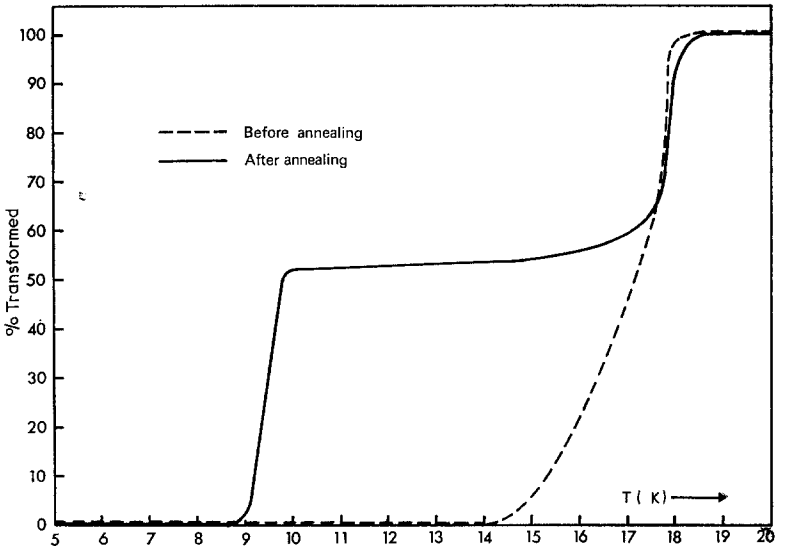

Figure 6 Comparison of T_c curves before and after high temperature annealing.

temperature at a given field we can find how much of the sample was above H_{c2} at that field. Similarly we can find the proportion with any given critical temperature. By putting the two sets of results together it is possible to find the value of H_{c2} corresponding to any particular T_c. These results have been reported previously [8] and so will not be repeated here, but use will be made of them in the discussion.

4.4. Annealing in argon

To obtain a more complete homogenization a series of specimens were annealed at a temperature of 1850°C. Al loss was significant at this temperature, and in order to minimize the loss annealing was carried out in argon at atmospheric pressure. They were then ordered at 750°C. These were specimens which had been tested previously after a 1500°C homogenization. After 3 h it was found that the width of the transition had decreased by about 30%. The narrowest transition observed was about 1 K. The highest current densities observed were about 2×10^5 A cm^{-2} at $2T$. These are about an order of magnitude greater than found in specimens annealed *in vacuo*. Linear signals in these specimens were not very meaningful as they were dominated by a thin surface layer, which had lost aluminium.

Under vacuum a specimen lost 11% of its aluminium after 3 h at 1850°C. This implies a diffusion coefficient of about 10^{-8} cm^2 sec^{-1} at this temperature for Al in Nb_3Al.

5. Discussion

5.1. A.c. measurements

The specimens in Fig. 2 conform to the pattern observed in other materials [9]. The first flux lines are unpinned by displacements of about 5 Å and the full critical state is reached for displacements of about 30 Å. These are rather smaller than those observed in Pb–Bi and NbTa [7, 10], as would be expected from the smaller values of ξ and the vortex spacing. In the absence of a detailed theory it is not possible to draw many further conclusions on the nature of the pinning centres from these results.

At high fields the behaviour was rather different. Firstly, the linear signal became very large (up to 30 or 40 μm) and sometimes dominated the behaviour. Secondly, the graph of restoring force against displacement did not tend to a constant value (see Fig. 3). Effects of this type have been observed in PbTl alloys [11] but they are only observed in the most reversible specimens after the surface barrier has been removed. The effects can be explained in PbTl by allowing for the fact that λ' is comparable with the radius. However, it is most unlikely that this is the explanation in Nb_3Al specimens having current densities of the order of 10^4 A cm^{-2} and no surface treatment.

The most likely explanation is that significant sections of the material are being driven normal in comparatively low fields. The flux penetrates into those normal regions which cut the surface giving an initial linear signal. The value of the

penetration measured depends on the geometry of the normal regions, but for a two dimensional model with a cycloidal interface the penetration measured is comparable to the size of the normal regions. It seems unlikely that the true situation differs greatly from this so that the observed penetration is consistent with a model in which there are normal regions of about 50 to 100 μm in size.

This is consistent with the microstructure of Fig. 1 which shows dendrites of about this size. It is worth pointing out that it is not sufficient just to have normal regions distributed in the material to produce this behaviour; the Pb–Bi eutectic for example contains 35% normal Bi precipitates. The essential feature is that the degraded A15 phases are superconducting in zero field, when the balancing is carried out, but go normal at higher fields. It seems that two distinct mechanisms producing linear signals must be recognized. One is the reversible oscillation of flux lines in superconducting materials, the other is the penetration of magnetic flux into genuinely normal regions of an inhomogeneous superconductor. The second mechanism bears a qualitative resemblance to the empirical model used by Kes *et al.* [12] to explain their results on pure niobium. They suggested a layer free of pinning at the surface to explain their linear signals, but this is an unlikely situation in pure niobium and their signals are almost certainly due to the first cause.

This hypothesis is confirmed by the measurements of T_c as a function of field [8]. If a specimen was powdered the signal from the mutual inductance coil showed that in samples with large bulk linear signals up to 50% of the powder would be normal at $2T$ and 4.2 K. The results showed the drop in H_{c2} was very much sharper than the drop in T_c. For example material with a critical temperature of 17 K had an upper critical field of only $2.5T$. It is clear that these regions of low critical field will prevent a material from carrying high current densities at high fields, and the critical current density is more dependent on the proportion of degraded material than the strength of the pinning.

5.2. Ordering in Nb_3Al

It is clear from Fig. 5 that within the A15 phase there is some variable which can modify T_c by 50% and H_{c2} by as much as a factor of ten. Some form of ordering process, or mean free path effect seems to be the only variable which would not show up more clearly in the phase diagram, but there are various possibilities for the type of disorder involved [1-3, 14].

Recent theoretical work by Somekh [15] has shown that if there are scattering centres on the niobium chains the density of states at the Fermi level is reduced and there is an extremely sharp drop in H_{c2}. The theory predicts a variation of T_c with H_{c2} which agrees reasonably well with the experimental results [8]. It is noticeable that alloys lie on this curve whether they are on the niobium-rich, or aluminium-rich, side of stoichiometry. These results are consistent with the suggestion of Courtney *et al.* [2] that degradation in Nb_3Sn is produced by vacancies on the niobium chains. These are supposed to occur, even on the niobium-rich side, because the niobium atoms migrate to the vacancies left by the tin atoms. Their X-ray measurements were not consistent with the hypothesis that the vacancies were only on the tin sites. We have made similar X-ray measurements, which are consistent with a similar model for Nb_3Al. The composition of a specimen with T_c of 9 K, interpreted using this model was:

Nb on Nb sites 68%
Nb on Al sites 6%
Al on Al sites 19%
Vacancies 7%.

Fig. 5 suggests that on the niobium-rich side there are two distinct materials, possibly with the same composition, with a sharp difference of about 6 K in T_c between them. Similar results were obtained by Courtney *et al.* in Nb_3Sn [2] and by Bachner and Gatos [1], and the latter suggest that it is caused by the ordering of vacancies along the niobium chains at a certain critical vacancy concentration of about 3%. Their main evidence for this is a decrease in lattice parameter, but we find in Nb_3Al the lattice parameter of the degraded phase is 2% larger, so it is probable that the lattice parameter changes are due to size effects. The niobium atom is about the same size as a tin atom, but larger than an aluminium, so an increase in parameter is expected if niobium goes on the aluminium sites.

As far as critical currents are concerned, the very low T_c material is irrelevant. Even material with a T_c of 17 K is still not very useful for practical purposes because H_{c2} is so low. Also regions of this type are useless as pinning centres because they do not have a sharp boundary with the superconducting material.

The mechanism proposed by Courtney *et al.* implies that to produce the degraded structure it is necessary to evaporate Sn from a high T_c material to leave vacancies on the Sn sites. We find, however, that alloys cooled from a melt contain degraded material, so clearly the structure with vacancies on niobium sites is the equilibrium structure, even in niobium-rich material. This is true of Nb_3Sn, as well as Nb_3Al. An ingot of Nb_3Sn was prepared in the same way as Nb_3Al and found to give very large linear signals. In contrast Nb_3Sn extracted from a commercial tape made by Plessey using the diffusion method had virtually no linear signal, showing that it was all high H_{c2} and T_c material.

Thus it is clear that, in principle, Nb_3Al will carry just as large critical currents as Nb_3Sn. However, it is essential that all degraded material be eliminated and the only hope of this seems to be to anneal at very high temperatures and pressures. Alternatively ways must be found, as have been done with Nb_3Sn, to prepare the material at low temperatures, without going through the peritectic.

6. Conclusions

(1) A.c. susceptibility measurements show that even after extensive heat-treatments Nb_3Al, cooled from the melt, contains significant amounts of material with a low critical field.

(2) The critical temperature drops off sharply when there are about 3% vacancies on the Nb chains, but H_{c2} is seriously reduced for much lower concentrations of vacancies.

(3) The results are consistent with the suggestion of Courtney *et al.*, that the effects are caused by vacancies on the niobium chains.

(4) In favourable conditions the critical current of Nb_3Al could be as high, or higher, than that of Nb_3Sn, but current densities at present are limited by the presence of low field material. It is more important to increase H_{c2} in a material, than to provide more pinning centres.

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