THE METALLURGICAL DESIGN OF Nb-Ti AND Nb3Sn MULTIFILAMENT SUPERCONDUCTORS

D. C. Larbalester*

ABSTRACT

Although the metallurgical properties are only one of a number of important concerns in the design of a useful multifilament magnet conductor, they are of basic importance both to the fabrication process and to the critical current density \( J_c \). In this paper we discuss some of the implications of making certain metallurgical choices - for example in the Nb-Ti system high \( J_c \) may be obtained over a range of alloy contents and for bronze route Nb3Sn conductors a variety of bronze to Nb ratios are chosen. Some of the consequences of the choice are explored with respect to the basic superconducting properties \( J_c \) and \( H_{c2} \), the strongly structure sensitive property \( J_c \), the fabricability and the mechanical stability.

NIOBIUM TITANIUM

Niobium titanium alloys have been the superconducting work horse for well over 10 years. However it is interesting to note that an ethnic diversity in standard compositions of Nb-Ti has emerged. At the low Ti end is IMI (UK) with Nb 44w/o Ti, the standard U.S. alloy, Nb 46.5w/o Ti, 11es in the middle while the Germans have generally preferred a higher Ti alloy, Nb 50w/o Ti. Standard tolerances on these alloys are generally ±2w/o so it can be seen that there is some overlap. Higher Ti alloys are sometimes also found e.g. Nb 53-55/w/o Ti but the original Atomics International high Ti alloy Nb 65w/o Ti has fallen into disfavor. By reference to the phase diagram shown in figure 1 it can be seen that a consequence of going to higher Ti contents is to make the body centered cubic (bcc) Nb solid solution phase B want to break down to a 2 phase mixture of \( \beta \) and a-Ti. At fields in the technical range of 0-9 Tesla and peak effects were common. Today commercial fine filament (10um dia. and greater) alloys can regularly be obtained with \( J_c \) in the 1750-2000 A/mm² (5T, 4.2K) range and literature values of up to 3600 A/mm² (5T, 4.2K) have been quoted. Such high values do not appear to be available from regular production. However we have obtained a production alloy from Vacuum Schmelze with \( J_c \) (5T, 4.2K) = 2700 A/mm². The full \( J_c/H \) curve for this and other commercial compositions of NbTi are shown in figure 2. Note however that a second nominal Nb 50w/o Ti alloy had \( J_c \) of only 1800 A/mm². Since the \( J_c \) is so strongly microstructure dependent these values need to be taken as guides rather than guarantees.

Our general understanding of how the microstructure of Nb-Ti alloys determines the \( J_c \) is good and this subject has recently been reviewed by McInerney. For the lower Ti alloys in the approximate range Nb 40-48w/o Ti \( \alpha \)-Ti rich precipitates are either not found or found in only small quantities. Here a high \( J_c \) requires the development of a highly dislocated cell structure produced by the large area reductions (generally > 10⁴:1) of wire drawing. Such a structure is shown in figure 3. A study by Neal et al. showed that \( J_c \) is proportional to the inverse of the cell size. Since the cell size is only slowly refined by wire drawing, such compositions need area reductions of between 10⁴-10⁵:1 to develop optimum \( J_c \) and fine filaments (10-25um dia.) are consequently preferred.

At higher Ti contents (the exact composition is variable depending on the 0 and N content, the heat treatment and the dislocation density) \( \alpha \)-Ti precipitation becomes an important factor. optimum \( J_c \) appears to be developed by sequential precipitation treatments (400°C) and draw cycles. Such treatments have been shown to nucleate very small \( \alpha \)-Ti precipitates 2-10nm in dia. within the cell walls and the double flux pinning effect of the cell wall structure and the high density of small \( \alpha \)-regions is responsible for the very high values of \( J_c \) obtained. The advantages of \( J_c \) shown by the well optimized Nb 50 Ti alloy are evident in figure 2. \( J_c \) being superior to the other alloys (46.5 and 53 Ti) at all fields. The principal advantage is however in the low and mid field range, declining towards \( H_{c2} \). At higher Ti contents the \( \alpha \)-Ti precipitates become progressively larger and the alloys more difficult to draw. The net effect is to make flux pinning by precipitates now the determinant of \( J_c \). High values of \( J_c \) can now be developed with less cold work and there is a tendency for the low field \( J_c \) to be relatively better than the high field \( J_c \).

Manuscript received September 26, 1978

*Department of Metallurgical Engineering, University of Wisconsin, Engineering Research Building, 1500 Johnson Drive, Madison, Wisconsin 53706.
Fabricability and Mechanical Stability

Of major importance to the cost and availability is the ability of a manufacturer to fabricate the composite with a minimum of special handling and a maximum of confidence. With presently available interstitial limits (O + C + N ≤ 1000 ppm max.), the low Ti alloys such as Nb 44-48 Ti are very evident distorted shape of the filaments and a Ti-rich reaction layer (1-3 pm) precludes the use of the electrical probe as a quantitative tool. In the binary system the phase exists over the range 18-25% Ti and the c is found to fall off sharply away from the stoichiometric Nb 25a/o Sn composition. Fortunately, when diffusion layers of Nb5Sn are grown, a substantial proportion of the layer is apparently at or near stoichiometry judging from the high values of Tc, Jc and Hc2 that can be achieved. Nb5Sn is also known to be sensitive to stress and in particular to the magnitude of the precompression exerted on them by the greater thermal contraction of surrounding bronze matrix 18-20. The c is depression of up to 1-1/2K from the bulk value of 18.2K are obtained when the ratio of bronze to Nb5Sn is very large. In FM conductors, however, as the Nb5Sn obtained, Jc and Hc2 appear to be sufficient to low values that bulk values of Jc (18-20) are obtainable.21

The situation with respect to Hc2 is less clear, few measurements of Jc being made above Hc2. For many reaction conditions Hc2 can be determined by making a linear extrapolation of JcHc2 vs. H to zero. We have found this function to be linear over the range 10-17 Tesla. The Hc2 value is found to depend both on the filament size, the degree of reaction and the heat treatment. Large ratio composites (e.g., bronze: Nb ratio 4:7:1) give lower maximum values of Hc2 (-20 Tesla) than those exhibited by composites with lower ratio (at 2.7:1 Hc2 can attain 22 Tesla). However it appears that the Hc2 of the high ratio composites can be made to approach that of the lower ratio by applying a suitable tensile stress.22 In doing so, the precompression exerted by the confining bronze matrix is reduced and the detrimental effect of compression on Tc and Hc2 removed. Although it is convenient to define these composites in terms of the known ratio of bronze to Nb, it is of course the bronze to Nb5Sn ratio that dominates the properties of the reacted composite. Except, however, in the case of fully reacted filaments of uniform composition, it is not easy to define this ratio.21 Hc2 and Tc are expected to increase with the extent of reaction, so long as the decreasing bronze: Nb5Sn ratio effect is not countered by the change of stoichiometric Nb5Sn to optimize properties to Sn deficient Nb5Sn of poorer properties. Such may occur for some compositions which do not completely react the Nb to stoichiometric Nb5Sn. This occurs for 13-18/o Sn bronze only when the bronze to Nb ratio falls below 3:1 by volume.

Critical Current Density

For FM Nb5Sn composites, the only microstructural feature responsible for flux pinning is the grain boundary23,24 and this gives a lopsided shape to the pinning force curve of Nb5Sn in comparison to Nb Ti (Fig. 5). Following Kramer,25 it appears that in the low field regime (< 8-9 Tesla), low temperature reaction treatments produce very fine grain sizes. However, since these conditions minimize grain growth and maximize the grain boundary cross-section. This is borne out by our measurements on the 4.61 Tesla: Nb ratio AERE composite (Fig. 7). At 600°C, Jc peaks at 1800 A/mm2 after 1250 hours reaction while at 750°C, the Jc peaks at 1650 A/mm2 after ~200 hours of reaction. All values of Jc quoted here are referred to the original bronze + Nb cross-section unless otherwise stated.

At high fields the grain structure is much less significant and the value of Hc2 appears to exert the dominating influence on Tc, i.e. in the 13-157 range. We have previously discussed the optimization of different bronze: Nb ratio composites for the high field range, concluding that for excess Sn composites (bronze: Nb ratio > 3:1) for 13-18/o
Figure 1. The Nb-Ti phase diagram

Figure 2. 4.2K critical current density versus field for 5 commercial Nb-Ti alloys.

Figure 3. Longitudinal section of the cell structure in Nb 49wt% Ti (courtesy A.M. West).

Figure 4. Cross-sections of regular 10μm dia Nb 46.5wt% Ti filaments and irregular ~50μm dia Nb 50.4wt% Ti filaments.

Figure 5. Pinning force curves for optimized FM Nb3Sn and NbTi conductors.

Figure 6. Critical current density versus field for Nb3Sn layers produced in different ways. Jc is referred to the Nb3Sn layer only.
Sn bronzes) the heat treatment temperature is not critical, providing substantial reaction takes place. Reactions which produce high Hc2 therefore automatically produce high Jc, unless they are grossly abusive. In a comparison paper to this,\textsuperscript{22} we present high field tensile stress measurements of Jc in the range of 13-16 Tesla, finding enhancements of over 100% in Jc for stresses of around 160 MPa. We also report there that very similar limiting values of Jc are obtained for 3 different composites from 3 different manufacturers. Qualitatively at least therefor the Jc properties of Nb3Sn are beginning to become well defined. On the one hand the zero external stress critical current Jc of a composite is maximized by having as much cross-section of Nb3Sn of stoichiometric chemical composition as possible, so that too high a bronze: Nb ratio and too low a filament area both to be avoided. In other applications, the desire to have maximum resistance to strain is dominant. Since this is encouraged by increasing the precompression on the Nb3Sn layers, low reactions, large bronze: Nb ratios and large filaments are favored. Such composites then require a tensile stress to attain their maximum values of Jc. The compromise is up to the individual magnet designer and since the extent of reaction is under his control, he can in principle get exactly what he wants.

In figure 6 we turn to consider the intrinsic Jc (measured across the Nb3Sn layer only) exhibited both by bronze route FM Nb3Sn and by tape Nb3Sn produced by CVD and by the liquid Sn route. The tape values are taken from\textsuperscript{25,26} while the FM values are derived assuming full conversion of the filaments to stoichiometric Nb3Sn and a Nb to Nb3Sn volume expansion of 37.5%.\textsuperscript{21} It is interesting to note that in tape Nb3Sn the Jc is also dominated by the relative thermal contractions of the substrate and Nb3Sn and that the highest Jc is obtained for Nb core tapes where the thermal contraction most closely matches the Nb3Sn. In the absence of external stress we too still reaction even with CVD Nb3Sn the remarkably high (but strictly experimental) values obtained with CVD Nb3Sn on Nb. In tension however the high field properties of FM Nb3Sn exceed those of the best reported tapes.

SUMMARY AND CONCLUSION

In many situation no choice is made of alloy composition and what is bought is what is available. However, there are some important differences in the areas in which the individual alloys excel and where it is possible choice may be worthwhile. Within the range Nb45-53Ti there is little change in Hc2 or Jc and there seems little reason to base a choice on this ground. If the prime requirement is for low AC loss, fine filaments will be required and single phase 8 alloy such as Nb44 or 46.5Ti will be preferable. For absolute maximum Jc, the choice will be Nb50Ti with some restriction on filament size. The higher Ti alloys become progressively more difficult to draw due to their increased hardness. However, since they develop high Jc without extensive cold work, they would be logical choices for some large dc cryostable magnets where large filaments can be tolerated.

For FM Nb3Sn application there still much less experience than for NbTi. Since for most people the brittle nature of Nb3Sn and the degradation produced by either electromagnetic strain or bending strain is the main concern, present applications may wish to emphasize conductors with high values of precompression. The choice will then favor large ratio conductors (3:4.5:1 B2:Nb), large filaments (5.8u diameter) and partial reaction. Such conductors should offer reasonable current density, (approximately 200 A/mm\textsuperscript{2} at 12T) together with the ability to give about 1% strain before critical current degradation is observed.\textsuperscript{27} For the adventurous, the choice will lie in the opposite direction, the reward being higher current densities with a lesser, though still adequate, margin of strain tolerance.

ACKNOWLEDGEMENTS

This work has been financially supported by the Department of Energy.

REFERENCES

22. S. O. Hong, D. C. Larbalestier, paper MA-1, this conference.