IEEE TRANSACTIONS ON MAGNETICS, VOL. MAG-15, NO. 1, JANUARY 1979

THE METALLURGICAL DESIGN OF Nb-Ti AND Nb_3Sn MULTIFILAMENT SUPERCONDUCTORS

D. C. Larbalestier*

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 discus 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 Nb_3Sn 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 T_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, lies 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 53-55w/o Ti but the original Atomics International high Ti alloy Nb 65w/o Ti has fallen into disfavor.[1] 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 β want to break down to a 2 phase mixture of β and α-Ti. At fields in the technical range of interest α-Ti is not superconducting and can be an efficient flux pinner. We explore some of the consequences of this phase instability in the sections that follow.

Basic Superconducting Properties

The first selection of an interesting superconducting magnet material is on the basis of suitably high values of T_c and H_{c2}. The T_c of the NbTi alloys is well known, lying in the range 9-9.3K for Nb 40-50w/o Ti,[2] although a value as low as 8.5K has been reported for an optimized conductor of Nb 49.9w/o Ti.[3] There has been more disagreement on the subject of H_{c2} although recent measurements are in agreement that H_{c2} attains maximum values of about 11 Tesla at 4.2K.[3,4] Reduced field values of H_{c2} for 4 commercial alloys are given in Table 1 from which it can be seen that H_{c2} is relatively independent of composition over the range 46.5-53w/o Ti. This is primarily because T_c and H_{c2} are determined by the composition of the β phase. Beyond about Nb 50 Ti α precipitation becomes increasingly important and tends to ensure that the matrix composition remains about Nb 48w/o Ti. Increases in H_{c2} over these values have to be achieved by going to ternary and quaternary compositions.[5]

TABLE I

H_{c2} Values of Commercial NbTi[4]

	1.5K	1.8K	2.K	4.2K
Nb 46.5w/o Ti	14.4 Tesla	14.1	13.9	11.1
49.7w/o Ti	14.3	14.0	13.8	11.0
50.4w/o Ti	14.2	13.9	13.7	10.9
52.7w/o Ti	14.1	13.8	13.6	10.9

Critical Current Density

In contrast to T_c and H_{c2} which are relatively fixed quantities the current density J_c is extremely structure sensitive and there has been continual progress in increasing J_c since the era of single filament NbTi when a J_c (5T, 4.2K) value of 1000 A/mm^2 was good and peak effects were common. Today commercial fine filament (10μm dia. and greater) alloys can regularly be obtained with J_c in the 1750-2000 A/mm^2 (5T, 4.2K)[4] range and literature values of up to 3600 A/mm^2 (5T, 4.2K) have been quoted.[8] Such high values do not appear to be available from regular production. However we have obtained a production alloy from Vacuumschmelze with J_c (5T, 4.2K) = 2700 A/mm^2. 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/mm^2. 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 McInturff.[9] For the lower Ti alloys in the approximate range Nb 40-48w/o Ti α-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 > 10^4:1) of wire drawing. Such a structure is shown in figure 3. A study by Neal et al[6] 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 10^4-10^5:1 to develop optimum J_c and fine filaments (10-25μm dia.) are consequently preferred.

At higher Ti contents (the exact composition is variable depending on the O and N content, the heat treatment and the dislocation density) α-Ti precipition becomes an important factor. Optimum J_c appears to be developed by sequential precipitation treatments (~400°C) and draw cycles.[7,8] Such treatments have been shown to nucleate very small α-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 α-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 α-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.[3,10]

Manuscript received September 26, 1978

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

0018-9464/79/0100-0209$00.75 © 1979 IEEE

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.)[6,11] the low Ti alloys such as Nb 44-48w/o are easily fabricable down to 10µm dia. filaments. High Ti alloys >55w/o Ti exhibit problems due to the presence of substantial 2nd phase.[9] The question of Nb 50w/o Ti is interesting. Reported methods of maximizing J_c are by giving multiple precipitation heat treatment and cold draw cycles.[3,8] A characteristic of at least some samples of this alloy is the very evident distorted shape of the filaments as may be seen in figure 4. Such composites show somewhat greater resistive slopes in their V/I characteristic compared to Nb 46.5 Ti. The general tendency appears to be that the finest filaments are most easily produced from single phase higher Nb alloys (Nb 44-46.5 Ti), the minimum filament diameter increasing as the Ti content does. The intermediate alloy Nb 50 Ti appears to pose some interesting fabrication problems and more published information on this subject would be useful. We are currently processing a billet of this material and will report on our findings at a later date.

Another aspect of the mechanical behavior of the Nb-Ti alloys is their response to stress at 4.2K. Discontinuous yielding and consequent heating of the Nb Ti into the normal state have been observed by a number of workers both for single phase β alloys, Nb 44 Ti, and the 2 phase Nb 50 Ti.[12,13] Various causes have been proposed including jerky dislocation flow, twinning or the martensitic breakdown of the β phase. A portion of the M_s curve (the temperature at which the transformation occurs solely on cooling) is shown in fig. 1 and it has been suggested that this extrapolates to a composition of Nb 49 Ti at 4K.[14] In other systems plastic deformation markedly enhances the transformation so it may be that the commercial alloys can be made unstable by stressing at 4.2K. All alloys (Nb 44-53 Ti) therefore appear potentially unstable to stress, the effect increasing as the Ti content increases. Magnet designers who are inclined towards the view that such phenomena may be a cause of training in high current density magnets may therefore prefer the higher Nb alloy conductors, due to their lesser tendency to instability.

NIOBIUM TIN

The development of filamentary (FM) Nb_3Sn conductors using the bronze route has greatly widened the applications for Nb_3Sn over those that can be met by the use of tape. The basic metallurgical device used to produce Nb_3Sn in filamentary form - that of co-drawing the ductile components of Cu or Cu-Sn alloy and Nb and deferring the formation of Nb_3Sn to an interdiffusion heat treatment at the final wire size is capable of a number of variants but we will confine our discussion here to the properties of bronze route multifilament composites. Mirroring the diversity of alloy contents found in Nb-Ti alloys, there is also important diversity in the design of FM Nb_3Sn conductors, most notably with respect to the bronze to Nb ratio and to the filament size. The significance that this has on determining the superconducting properties is considerable and we here discuss some of the consequences.

Basic Superconducting Properties

In considering the properties of Nb_3Sn, the composition of the phase is important. However, reliable values are seldom obtained, especially in fine filamentary form, because the extreme thinness of most reaction layers (1-3µm) precludes the use of the electron probe as a quantitative tool. In the binary system the phase exists over the range 18-26a/o Sn[16] and the T_c is found to fall off sharply away from the stoichiometric Nb 25a/o Sn composition.[17] Fortunately, when diffusion layers of Nb_3Sn are grown, a substantial proportion of the layer is apparently at or near stoichiometry judging from the high values of T_c, J_c and H_{c2} that can be obtained. T_c and H_{c2} are 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] T_c depressions of up to 1-1/2K from the bulk value of 18.2K are obtained when the ratio of bronze to Nb_3Sn is very large.[19] In FM conductors, however, as the Nb_3Sn layer grows the precompression declines to sufficiently low values that bulk values of T_c (18-18.2K) are obtainable.[21]

The situation with respect to H_{c2} is less clear, few measurements of J_c being made up to H_{c2}. For many reaction conditions H_{c2} can be determined by making a linear extrapolation of $I_c^{1/2}$ vs. H to zero. We have found this function to be linear over the range ~ 10-17 Tesla. The H_{c2} 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 H_{c2} (~ 20 Tesla) than those exhibited by composites with lower ratio (at 2.7:1 H_{c2} can attain 22 Tesla).[15] However it appears that the H_{c2} of the high ratio composites can be made to approach that of the lower ratio by applying a suitable tensile stress.[22] In so doing, the precompression exerted by the confining bronze matrix is reduced and the detrimental effect of compression on T_c and H_{c2} 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 Nb_3Sn ratio which 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] H_{c2} and T_c are expected to increase with the extent of reaction, so long as the decreasing bronze: Nb_3Sn ratio effect is not countered by the change of stoichiometric Nb_3Sn of optimum properties to Sn deficient Nb_3Sn of poorer properties. Such may occur for composites where there is insufficient Sn to completely react the Nb to stoichiometric Nb_3Sn. This occurs for 13w/o Sn bronzes only when the bronze to Nb ratio falls below 3:1 by volume.

Critical Current Density

For FM Nb_3Sn composites, the only microstructural feature responsible for flux pinning is the grain boundary[23,24] and this gives a lopsided shape to the pinning force curve of Nb_3Sn 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 on fine filaments produce the highest J_c since these conditions minimize grain growth and maximize the grain boundary cross-section. This is borne out by our measurements on the 4.6:1 bronze: Nb ratio AERE composite CF87:[15,21] at 600°C J_c (5T) increases monotonically with time, reaching a value of 1800 A/mm^2 after 1250 hours reaction while at 750°C the J_c peaks at 1650 A/mm^2 after ~200 hours of reaction. All values of J_c 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 H_{c2} appears to exert the dominating influence on J_c, even 5-7 Tesla below H_{c2}, i.e. in the 13-15T 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 13w/o

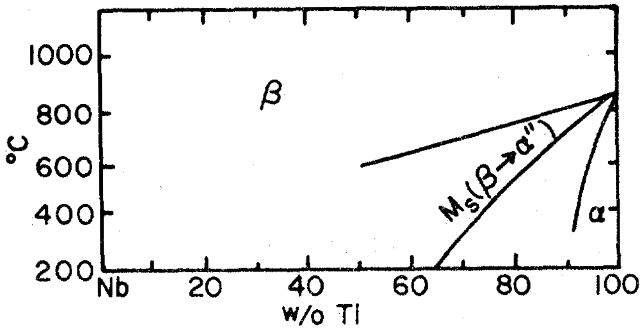


Figure 1. The Nb-Ti phase diagram

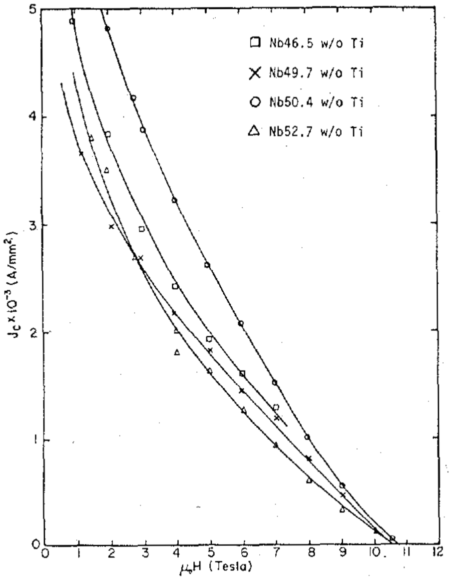


Figure 2. 4.2K critical current density versus field for 4 commercial Nb-Ti alloys.

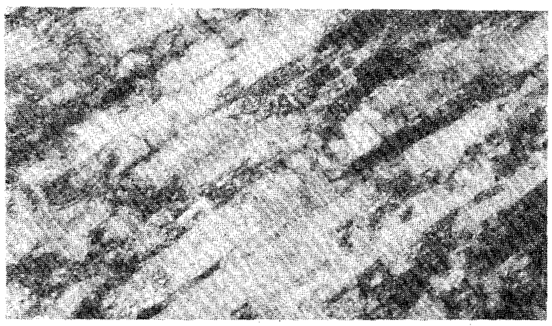


Figure 3. Longtitudinal section of the cell structure in Nb 48w/o Ti (courtesy A.W. West).

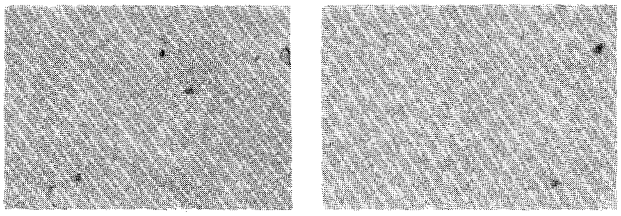


Figure 4. Cross-sections of regular 10μm dia Nb 46.5w/o Ti filaments and irregular ~50μm dia Nb 50.4w/o Ti filaments.

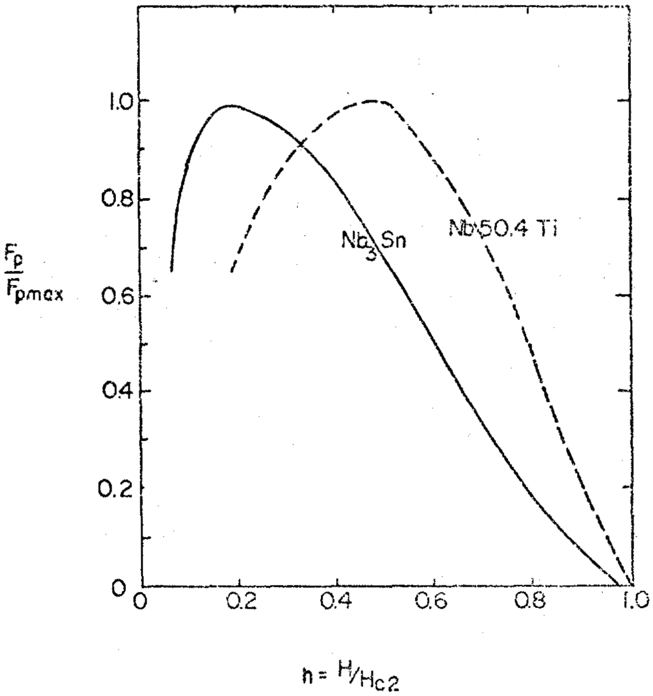
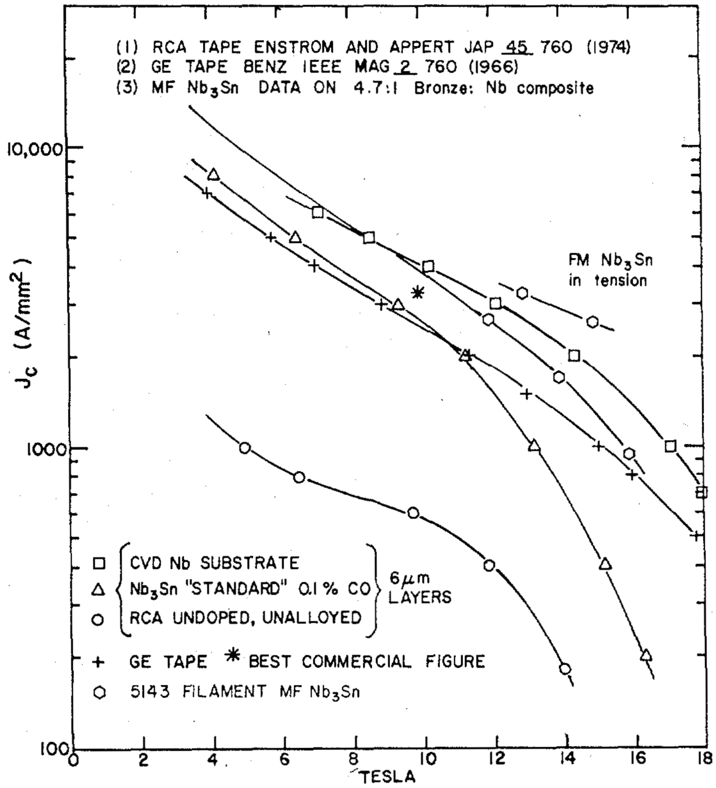


Figure 5. Pinning force curves for optimized FM Nb_3Sn and NbTi conductors.



J_c FOR Nb_3Sn LAYERS PRODUCED IN DIFFERENT WAYS.

Figure 6. Critical current density versus field for Nb_3Sn layers produced in different ways. J_c is referred to the Nb_3Sn layer only.

Sn bronzes) the heat treatment temperature is not critical, providing substantial reaction takes place. Reactions which produce high H_{c2} therefore automatically produce high J_c, unless they are grossly abusive.[15] In a comparison paper to this,[22] we present high field tensile stress measurements of J_c in the range of 13-16 Tesla, finding enhancements of over 100% in J_c for stresses of around 160 MPa. We also report there that very similar limiting values of J_c are obtained for 3 different composites from 3 different manufacturers. Qualitatively at least therefore the J_c properties of Nb_3Sn are beginning to become well defined. On the one hand the zero external stress critical current I_c of a composite is maximized by having as much cross-section of Nb_3Sn of stoichiometric chemical composition as possible, so that too high a bronze: Nb ratio and too low a reaction are 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 Nb_3Sn 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 J_c. 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 J_c (measured across the Nb_3Sn layer only) exhibited both by bronze route FM Nb_3Sn and by tape Nb_3Sn produced by CVD and by the liquid Sn route. The tape values are taken from[25,26] while the FM values are derived assuming full conversion of the filaments to stoichiometric Nb_3Sn and a Nb to Nb_3Sn volume expansion of 37.5%.[21] It is interesting to note that in tape Nb_3Sn the J_c is also dominated by the relative thermal contractions of the substrate and Nb_3Sn and that the highest J_c is obtained for Nb core tapes where the thermal contraction most closely matches the Nb_3Sn. In the absence of external stress we have still not achieved with FM Nb_3Sn the remarkably high (but strictly experimental) values obtained with CVD Nb_3Sn on Nb. In tension however the high field properties of FM Nb_3Sn 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 excell and where it is possible choice may be worthwhile. Within the range ~Nb45-53Ti there is little change in H_{c2} or T_c 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 β alloy such as Nb44 or 46.5Ti will be preferable. For absolute maximum J_c, 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 J_c without extensive cold work, they would be logical choices for some large dc cryostable magnets where large filaments can be tolerated.

For FM Nb_3Sn application there still much less experience than for NbTi. Since for most people the brittle nature of Nb_3Sn 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 Bz:Nb), large filaments (5-8μ diameter) and partial reaction. Such conductors should offer reasonable current density, (approximately 200 A/mm^2 at 12T) together with the ability to give about 1% strain before critical current degradation is observed.[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.[15]

ACKNOWLEDGEMENTS

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

REFERENCES

1. J. B. Vetrano, R. W. Boom, JAP 36, 1179, (1965).
2. J. K. Hulm, R. D. Blaugher, Phys. Rev., 123, 1569 (1961).
3. H. Hillmann, K. J. Best, IEEE Trans. Mag., 13, 1968 (1977).
4. K. F. Hwang, D. C. Larbalestier, Paper FB-6 this conference.
5. See for example M. Suenaga, K. Ralls, JAP, 40 4457, (1969).
6. D. F. Neal, A. C. Barber, A. Woolcock, J. Gidley, Acta Met., 19, 143, (1971).
7. I. Pfeiffer, H. Hillmann, Acta Met., 16, 1429, (1968).
8. J. Willbrand, W. Schlump, Z. Metallkunde, 66, 714, (1975).
9. A. D. McInturff to appear in "The Metallurgy of Superconducting Materials", ed. T. Luhman and D. Dew-Hughes.
10. A. D. McInturff, G. Chase, JAP 44, 2378, (1973).
11. T. E. Cordier, W. McDonald, IEEE Trans. Mag. 11, 280 (1975).
12. D. Evans, Rutherford Laboratory Report, RL-73-092, (1973).
13. G. Pasztor, C. Schmidt, JAP 49, 886 (1978).
14. C. C. Koch, D. S. Easton, Cryogenics, 17, 391 (1977).
15. D. C. Larbalestier, Proc. of 6th Int. Conf. on Magnet Techology MT-6 1080 (1977).
16. D. E. Madsen, AERE Harwell Report No. 6347, (1970).
17. J. J. Hanak, RCA Review, 25, 3, (1964).
18. M. Suenaga, W. B. Sampson, BNL Rep. 16415, (1972).
19. L. Luhman, M. Suenaga, K. Klamut, to appear in 24 Adv. in Cryogenic Eng. (1978).
20. G. Rupp, IEEE Trans. Mag. 13 1565 (1977).
21. D. C. Larbalestier, P. E. Madsen, J. A. Lee, M. N. Wilson, J. P. Charlesworth, IEEE Trans. Mag. 11, 247, (1975).
22. S. O. Hong, D. C. Larbalestier, paper MA-1, this conference.
23. A. West and R. Rawlings, J. Mat. Sci. 12, 1862, (1974).
24. R. M. Scanlan, W. A. Fictz, E. F. Koch, J.A.P., 46, 2244, (1975).
25. M. G. Benz, IEEE Trans., MAG, 2, 760, (1966).
26. R. E. Enstrom, J. R. Appert, J.A.P., 45, 760, (1974).
27. D. W. Deis, D. N. Cornish, A. R. Rosdahl, D. G. Hirzel, Proc. of 6th Inst. Conference on Magnet Technology MT-6 1028, (1977).