FURTHER INVESTIGATIONS OF THE UPPER CRITICAL FIELD AND THE HIGH FIELD CRITICAL CURRENT DENSITY IN Nb-Ti AND ITS ALLOYS

David G. Hawksworth and David C. Larbalestier
Materials Science Center and Dept. of Metallurgy
University of Wisconsin
Madison, WI 53706

Summary

The work described in this report was undertaken, within the context of the 12 Tesla program, to investigate the possibility of increasing the upper critical field, Hc_2, of Nb-Ti through alloying additions. A preliminary report has previously been given by us[1]. In the first part of this paper we report further measurements of Hc_2 in the Nb-Ti-Ta and Nb-Ti-Hf systems. Whilst we find only small enhancements of $\sim$0.3 Tesla in $\mu_o Hc_2$ (4.2K) compared to binary Nb-Ti, at 2K there is a wide composition range in the Nb-Ti-Ta system where $\mu_o Hc_2$(2K) exceeds 15 Tesla, reaching a maximum of 15.5 Tesla. This represents an enhancement of 1.3 Tesla over unalloyed Nb-Ti. By comparison alloys in the Nb-Ti-Hf system show a maximum enhancement in $\mu_o Hc_2$(2K) of only 0.3 Tesla. The reasons both for the enhancements in Hc_2 and for the differences in behavior shown by alloys containing Ta and Hf are briefly discussed.

In part II we discuss common features in the behavior of the high field critical current density, J_c, of four commercial Nb-Ti composites and upon the basis of this behavior predict the enhancements in high field J_c to be expected from using Nb-Ti-Ta and its alloys.

I. The Upper Critical Field of the Nb-Ti-Ta and Nb-Ti-Hf Systems

Introduction

The upper critical field in the absence of paramagnetic limitation at 0 K is given by the Ginzburg, Landau, Abrikosov and Gorkov (GLAG) theory(2) as:

$$\mu_o H\overset{*}{c}_2(0) = 3.1 \times 10^3 \, \gamma \, \rho_n \, T_c \quad \text{(Tesla)} \qquad (1)$$

where γ is the electronic specific heat coefficient, ρ_n, is the normal state resistivity and T_c the critical temperature. Werthamer, Helfand and Hohenberg (WHH)(3) showed that $\mu_o Hc_2(0)$ could also be expressed as

$$\mu_o H\overset{*}{c}_2(0) = 0.69 \mu_o \, T_c \, (dHc_2/dT)_{T_c} \; . \qquad (2)$$

$\mu_o Hc_2(0)$ should reach 17-18 Tesla in binary Nb-Ti alloys instead of the 14-15 Tesla observed. The origin of the diminished Hc_2 lies in the appreciable orbital paramagnetism of Nb-Ti which makes a significant contribution to the free energy of the normal state. This paramagnetic limitation can be relaxed by spin-orbit scattering processes and the theory of WHH(3) considers this in detail.

The rate of spin-orbit scattering is proportional to the fourth power of the average atomic number of the alloy and for this reason we have focussed our attention on the Nb-Ti-Hf and Nb-Ti-Ta systems. The heavy element additions of hafnium (Z=72) and tantalum (Z=73) should significantly reduce the paramagnetic limitation upon Hc_2 of Nb-Ti.

Experimental Details

Alloys were prepared, using industrial grade starting materials, by arc melting in an argon atmosphere[1]. Our alloys were homogenized for 8 hours at 1350°C following arc melting, cold rolled by about 75%, recrystallized for 1 hr at 875°C (up to 1000°C for the Nb-Ti-Ta samples), water quenched and then sheathed in copper before being cold drawn to an area reduction ratio of 100:1. The Hc_2 measurement was performed resistively on these 1mm dia. wires at a measuring current density of 0.05 A/mm^2, the first onset of resistance being using to define Hc_2.[1] As we have discussed elsewhere, it is difficult to make an unambiguous definition of Hc_2 and all characterizations of upper critical field by a single value are arbitrary[4,5]. Depending on the choice of point on the resistive transition curve and the value of measuring current density, Hc_2 can vary by approximately ± 3/4 T. Measurements of Hc_2 at 4.2K and below were performed at the Francis Bitter National Magnet Laboratory and those at temperatures greater than 4.2K in an experiment which fits a 7 Tesla solenoid in our own laboratory[1].

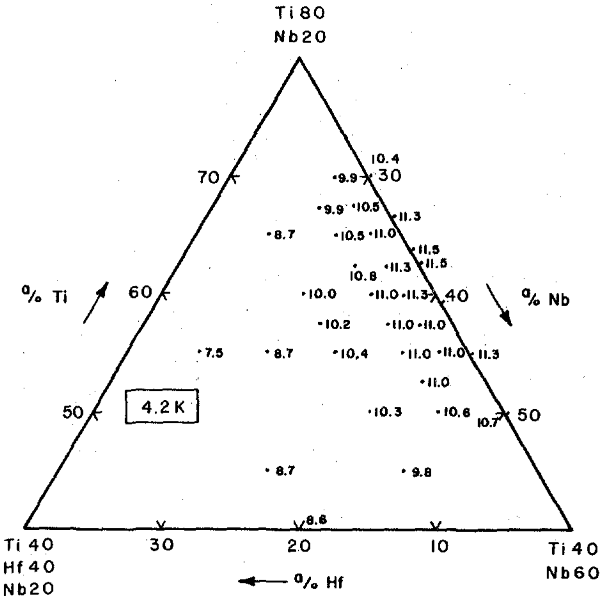

Fig. 1: Upper critical field of Nb-Ti-Hf alloys at 4.2 K.

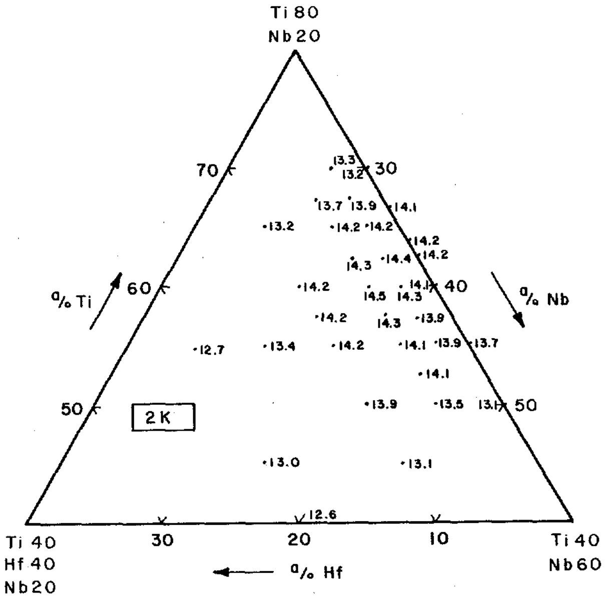

Fig. 2: Upper critical field of Nb-Ti-Hf alloys at 2 K.

The upper critical field values for Nb-Ti-Hf at 4.2 and 2 K in the β state (quenched from 875°C) are shown in Figs. 1 and 2. Alloys in the Nb-Ti-Hf system appear to show a steady decline in Hc_2 at 4.2 K as Hf is substituted for Ti. At 2 K, however, there is a small increase in μ_oHc_2, from 14.2 T in the binary alloys to 14.5T for an alloy of composition Nb60 at % Ti 5 at % Hf (Nb41wt%Ti 13wt% Hf). These increases though of fundamental interest are not sufficiently large to be of practical interest. Some details of the upper critical field in the Nb-Ti-Ta system have already been given.[1] In anticipation of a fuller report of the physical and superconducting properties, we recall that there is a large range of alloys for which upper critical field values greater than 15 T at 2 K are found. The peak value is 15.5 T for alloys in the neighborhood of Nb 65at%Ti 12.5at%Ta (Nb 42wt%Ti 19 wt% Ta). This composition is a little less Ta-rich [7] than the alloy chosen for the General Atomics 12 Tesla coil, whose μ_oHc_2 value is also 15.5T. The initial increase in Hc_2 with Ta addition is quite steep, μ_oHc_2 values greater than 15T being obtained for Ta additions of ∿5 at % (∿12wt%). A fuller report of these results, as well as those on the partial substitution of Ta by cheaper Hf, is also in preparation.[6] At 4.2K the increase in Hc_2 is less marked, being about 0.3T for alloys in the neighborhood of Nb60 at%Ti7.5at%Ta (NB40wt%Ti19wt%Ta). A previous report of larger enhancements in the Hc_2 at 4.2 K appears to be due to the fact that different definitions of Hc_2 were used for the binary and ternary alloys.[8]

In order to reach a fundamental understanding of the behavior of the upper critical field when Ta or Hf additions are made to Nb-Ti, we have used measured values of ρ_n, T_c and $(dHc_2/dT)_{T_c}$ to calculate $Hc^*_2(0)$ and γ using equations 1 and 2 for a series of Nb-Ti-Hf and Nb-Ti-Ta alloys of constant electron to atom ratio. These results will be reported in detail elsewhere and we provide only a summary of our findings here.[6]

Substitution of Hf for Ti is found to increase ρ_n but γ and T_c fall more rapidly so that $Hc^*_2(0)$ is decreased. In the Nb-Ti-Ta alloys, however, substitution of Ta for Nb leaves ρ_n and γ essentially unchanged whilst T_c falls only slowly; $Hc^*_2(0)$ therefore decreases only gradually. The effect of increased spin-orbit scattering with increasing Hf or Ta content appears in the comparison of the experimental and GLAG nonparamagnetically limited critical fields at 2 K. In the binary Nb-Ti alloy the experimental μ_oHc_2 lies ∿2 Tesla below the GLAG value. However, as the Ta or Hf content of the alloy is increased the experimental Hc_2 values more closely approach the GLAG limit, appearing to exceed these limits for Hf and Ta contents greater than 12at%[6].

II. Scaling Behavior and High Field J_c

Given the enhancements found in the upper critical field of Nb-Ti-Ta alloys at low temperatures, the added expense of Ta additions and the well-known sensitivity of the critical current density to the processing and heat treatment conditions, it is desirable to enquire whether the J_c of these alloys can be accurately predicted. This is a matter we have recently reported upon[9] and here we consider further extensions and implications of this work.

The development of high J_c in Nb-Ti composites requires the development of an optimum, strong pinning, microstructure. A prerequisite has been shown to be the development of a fine scale (<50nm) dislocation sub-band structure and the highest critical current densities are obtained when this is accompanied by fine scale precipitation of α-Ti in the sub-band walls.[4,5,10] There is much, however, that is still uncertain about the processing of Nb-Ti composites to high J_c values and the introduction of new alloys has led to some expressions of concern. We have recently made careful studies of a variety of commercial composites, of different compositions, manufacture and J_c value in order to understand the variation of properties met with in commercial practice.[9] The correlation between high J_c and optimum pinning microstructure is best described in terms of the volume pinning force $F_p=J_c x B$. It is well-known that the pinning force curve for a particular material has a unique shape, depending on the alloy microstructure, and that it also scales with temperature obeying a relation[11]:

$$F_p = J_c \times B = f(h)\ Hc_2{}^n(T) \qquad (3)$$

where n is an empirically determined index and f(h) is the shape of the pinning curve.

In (9) we performed a detailed analysis of the scaling behavior in four commercial high current density Nb-Ti composites and applied this to the prediction of the high field J_c of a Nb65a/oTi 10a/oTa (Nb43wt%Ti 25wt%Ta) alloy such as has been chosen for the General Atomics 12 Tesla coil.[7] Although the absolute values of the pinning force curves of the different composites were rather different the reduced pinning curves F/F_{pmax} vs. $h(=H/Hc_2)$ of all four composites were found to be rather similar, as is shown in Fig. 3 and all were found to scale with temperature. At high fields, h > ∿0.7-0.75, F_p is proportional to (1-h), a fact that makes the high field J_c particularly easy to predict. Our predictions of J_c, shown in Fig. 4, were made solely on the basis of the increased upper critical field and an assumption that the microstructure could be optimized to the range of levels found for large volume commercial conductors[9]. Also shown in Fig. 4 is the value actually obtained by MCA[7] on a multifilamentary billet of Nb43wt%Ti 25wt%Ta. We have derated the reported value of J_c=700 A/mm^2 by 10% since we showed in (9) that a constant voltage criterion of

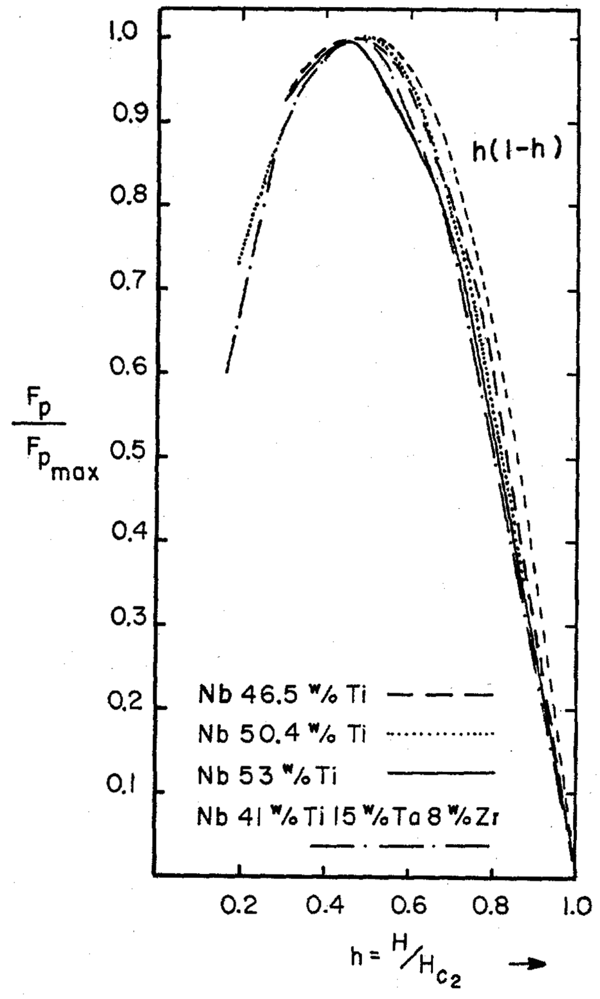

Fig. 3: Reduced pinning force curves for four differently optimized commercial Nb-Ti composites.

1 µV/cm can seriously overestimate the true J_c at fields close to Hc_2. The agreement between the predicted and measured J_c values for the Nb-Ti-Ta alloy is excellent, considering that our prediction was made on the basis for a 30 gm laboratory ingot and that the multifilamentary billet was processed industrially quite independently from us. More surprisingly, perhaps, the J_c of alloyed Nb-Ti at 2 K exceeds that of Nb_3Sn at any temperature, even though 12 Tesla represents about 80% of the upper critical field of the Nb-Ti-Ta alloy and only about 50% of that of Nb_3Sn. This points to the extremely strong nature of the pinning microstructure in Nb-Ti alloys.

High Field J_c Optimization

There is a considerable spread in the predicted J_c values shown in Fig. 4, corresponding to the range of J_c values commercially available. (The best may exceed the average by 30-50%, even at 5 T, 4.2 K.) High J_c values are particularly interesting to designers of high current density magnets. One new potential user is the constructor of 8-10 T accelerator dipoles. In this case it is preferable to focus on the data of Fig. 3, replotted so as to show the differences in magnitude of $F_p(h)$, as in Fig. 5 (the composition is less important than the optimization, compositions being given for identification only). A particularly important feature of Fig. 5 is that not only does the

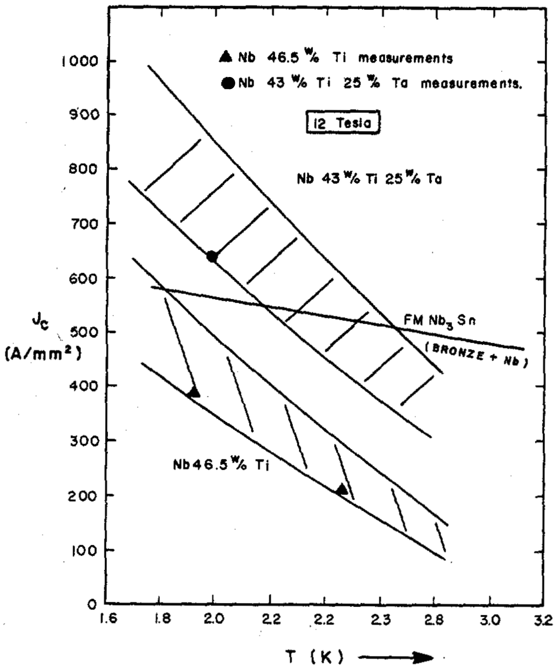

Fig. 4: Predicted and measured values of J_c (12 Tesla) in Nb46.5wt%Ti and Nb43wt%Ti 25wt%Ta.

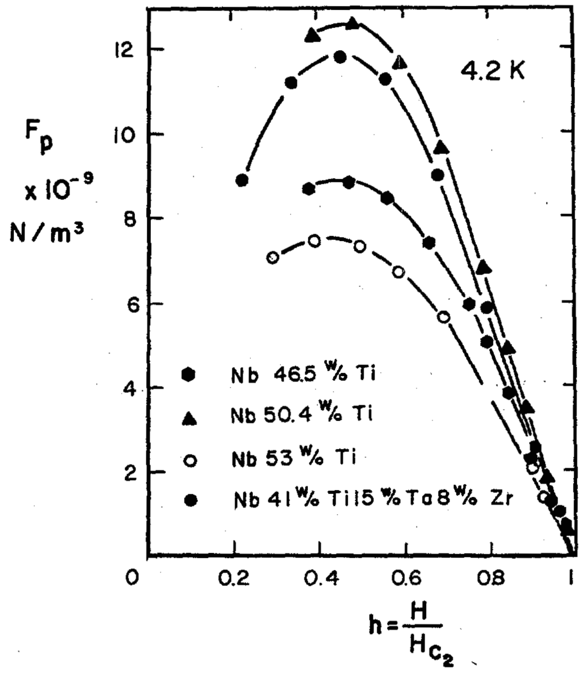

Fig. 5: The absolute pinning force for the conductors previously described in Fig. 3.

magnitude of F_p(max) differ from conductor to conductor but so also does the high field slope. This is a rather convenient result, since most optimization studies have been performed at 5 T, 4.2 K (close to F_{pmax}) and this will also serve for high field use too.

Of the 4 commercial flamentary composites for which data is given in Fig. 5, only the Nb-Ti-Ta-Zr alloy has a different Hc_2. In this case the low and mid-field J_c is excellent and high values of J_c appear to be achievable with lower degrees of cold-work than with alloys such as Nb46.5wt%Ti.[13] However, in spite of the Ta content, the Hc_2 is about 1 T lower than the best binary Nb-Ti alloy so that above 7 T at 4.2 K its J_c falls off very sharply. J_c plots for these alloys have been presented previously.[5,9] It is instructive however, to normalize Fig. 5 by dividing F_p by $(H_{c2})^2$ When this is done, as in Fig. 6, the very strong pinning of the quaternary alloy becomes evident. Large low field J_c values have frequently been associated with Nb-Zr alloys - in this case 8wt%Zr appears to exert a marked influence. Osamura et al.[12] have made a recent microstructural study of this alloy. They find that the precipitates of α-Ti/Zr are more closely spaced than in a binary alloy of Nb48wt%Ti. Thus, the maximum J_c values may be found by either adjusting the quaternary Cryozitt alloy to slightly higher e/a (at present it is on the Ti rich side of the Hc_2 plateau at e/a 4.32) or by adding ∼5wt%Zr to the Nb43wt%Ti 25wt%Ta alloy. The high plateau of Hc_2 around this alloy composition should ensure that the matrix Hc_2 remains high, irrespective of α-Ti/Zr precipitation, and the strong pinning of the Zr additions should increase J_c at all field levels.

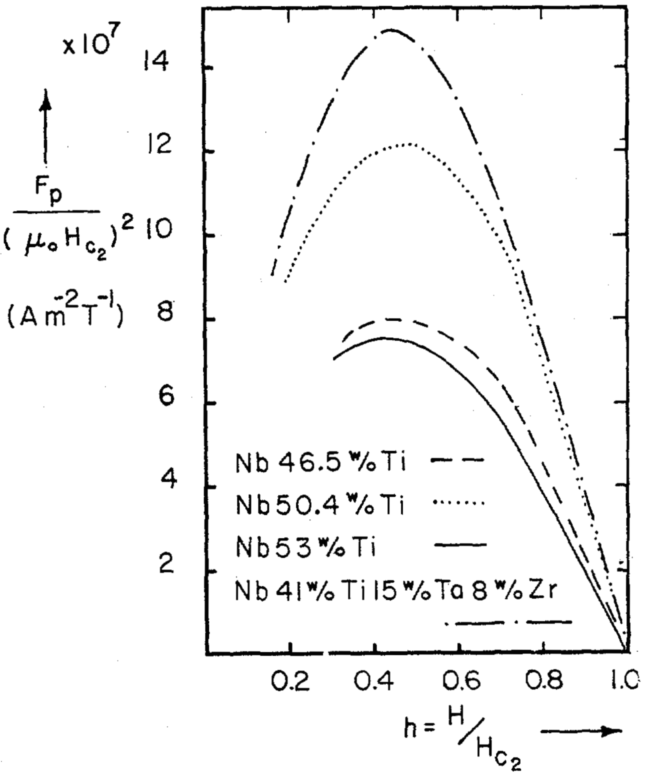

Fig.6: The pinning force normalized by the square of the upper critical field.

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