COMPOSITIONAL INHOMOGENEITIES IN Nb-Ti AND ITS ALLOYS

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Abstract

Results are presented showing that commercially produced Nb-Ti and Nb-Ti-Ta can have extensive chemical inhomogeneities, of order 10 wt.%. These chemical inhomogeneities are associated with significant sub-structure irregularities and, in one case, with filament sausaging and poor J_c performance. Homogenization of such alloys is discussed. Some recent ingots have been much more homogeneous than those first studied and it is concluded that purchase of chemically homogeneous materials is preferred for high J_c composites.

Introduction

Many aspects of the production of Nb-Ti are subject to stringent control; for example, the chemical specification, the grain size, the inclusion count, the surface roughness and the straightness of the rods destined for billet packing. The chemical specification is rather strict; the normal U.S. alloy, Nb 46.5 wt.% Ti, has a Ti tolerance of ± 1.5 wt.% Ti and is permitted only 200 ppm maximum of most (except Ta and O) impurities.[1] However, the separation between solidus and liquidus is rather large in the Nb-Ti system and this leads to the possibility of significant local chemical segregation (coring) in cast alloys. This has been recognized by a number of manufacturers.[2,3] One report on the manufacture of large Nb-Ti ingots states that the coring in a 0.4 m dia Nb 46.5 wt.% Ti ingot was on a scale of ~ 100 μm with a composition spread of about 6 wt.% Ti.[2] Coring has received very little published study, however, and it is not clear whether the above figures are at all typical.

The present paper describes some observations on the extent of and the effects of coring on the microstructure and properties of Nb-Ti and Nb-Ti-Ta alloys. Our studies of this subject were triggered by two parallel investigations. One of these concerned the study of the rate of sub-band refinement in Nb 46.5 wt.% Ti during cold work and our surprise at the irregular sub-band structures which were produced in the material under study. The second of the studies was performed on the second billet of Nb 43 wt.% Ti 25 wt.% Ta produced by Wah Chang and MCA.[4,5] Considerable filament sausaging was found in this billet and the critical current was smaller than expected. In both of these cases, considerable local chemical inhomogeneities were found. Consideration of the present results suggests that coring of varying extent is present in all Nb-Ti alloys and that removing or minimizing it requires special, but feasible, manufacturing steps. It is concluded that this effect may be one of the major causes of product variability in composite manufacture.

I. Sub-band Structure Development in Alloy Rods

Experimental Procedure

These studies were initiated with 15.9 mm diameter rods of Nb 46.5 wt.% Ti and Nb 43 wt.% Ti 25 wt.% Ta taken from Teledyne Wah Chang's normal production. The scale of the initial ingots differed substantially, the binary alloy having been melted on a large scale[2] (0.5 m dia) while the ternary was a special melt (0.15 m) for the General Atomics 12 Tesla test coil.[6] The rods had last been annealed at 40 mm diameter, before being swaged to the size at which they were delivered to us. The rods were sheathed in copper before drawing, the starting diameter being increased from 15.9 mm to 19 mm. (All rod diameters now quoted refer to the total diameter of the Nb-Ti rod and the copper sheathing.) The rods were then drawn down to a final diameter of 2.7 mm with an area reduction of 20% at each pass. Samples for TEM examination were cut from the back-end of the rod after each pass. Discs were cut from each sample of the rod for examination of the microstructure in transverse section. Thin foils for TEM were prepared using a commercially available electropolishing unit. Details of the electropolishing conditions for Nb-Ti alloys have been given previously.[7]

Selected samples of the drawn rod were heat-treated for 100 hours at 400°C (after removal of the copper sheathing) to determine what effect the drawn microstructure had on the size and morphology of the α-Ti particles which precipitated during the heat-treatment.

Results

Fig. 1 shows the microstructure of the drawn Nb-Ti rod at 16.5 mm diameter (cold area reduction ratio (CARR) = 6.32, true strain (ε) = 1.84). The rod contained a high density of dislocations, but the sub-band structure had not yet started to develop. On further drawing to 6.7 mm diameter, Fig. 2, a transverse section of the microstructure showed that long, narrow sub-bands had developed in certain areas of the rod but not in others (CARR = 50.8, ε = 3.93). This inhomogeneous microstructure was still present at the final diameter of 2.7 mm, Fig. 3 (CARR = 313, ε = 5.75).

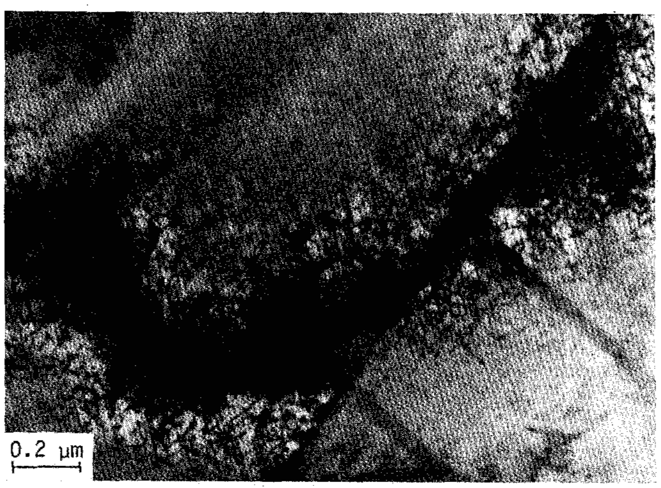

Fig. 1. Nb-Ti rod drawn to 16.5 mm diameter

The transverse microstructure of the rod at 2.7 mm diameter after heat-treatment for 100 hours at 400°C

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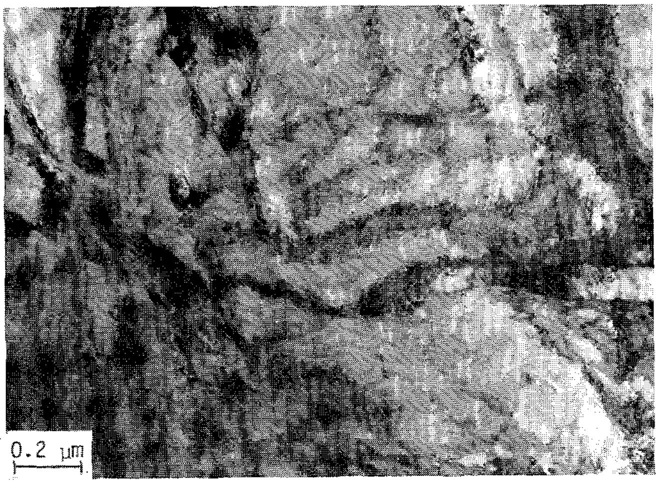

Fig. 2. Nb-Ti rod drawn to 6.7 mm diameter.

Fig. 3. Nb-Ti rod drawn to 2.7 mm diameter.

is shown in Fig. 4. The elongated sub-bands of Fig. 3 had become far more equi-axed after heat-treatment but there was a large variation in the morphology of the α-Ti precipitates. Large, equi-axed precipitates were present in the area containing sub-bands, but in the region free of sub-band structure, the α-Ti precipitates were small discs orientated with respect to the matrix. The variation in the α-Ti precipitate morphology with the degree of cold-work in the matrix has been reported previously.[7]

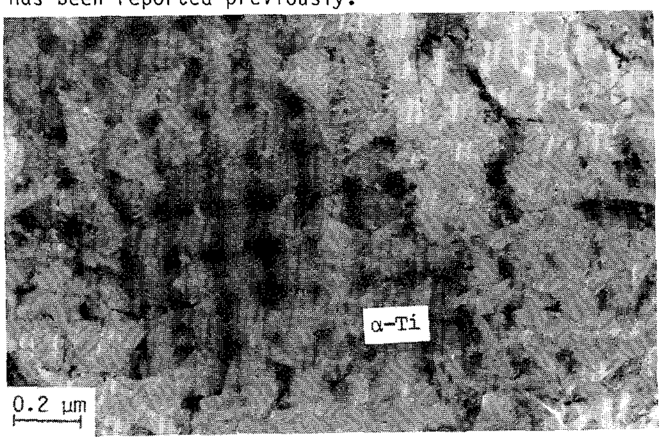

Fig. 4. Nb-Ti rod at 2.7 mm diameter. Heat-treated for 100 hours at 400°C.

II. Measurement of Compositional Inhomogeneities

Experimental Procedure

Samples of both rods were examined in the as-received condition (i.e. after cold-working from 40 mm to 15.9 mm by Wah Chang), together with cross-sections of the composite fabricated by MCA from the Nb 43 wt.% Ti 25 wt.% Ta ingot, as well as a Nb 46.5 wt.% Ti composite of similar design (both were of the Fermilab design). The Nb 46.5 wt.% Ti composite bore no known relation to the rod of Nb 46.5 wt.% Ti, however, and was included only for control purposes.

Sections were cut from the rods and the multifilamentary composites and mounted in Bakelite. The samples were ground and polished but not etched. All the samples were examined in a JEOL 35C scanning electron microscope (SEM) with an energy dispersive x-ray (EDX) spectroscopy detector attachment. The rod samples were imaged in the SEM using the back-scattered electron signal. The back-scatter image is very sensitive to differences in the average atomic number between different regions of the sample and is useful for detecting compositional inhomogeneities. Regions of higher average atomic number back-scatter more electrons from the incident beam and thus appear lighter in the back-scatter image.

Results

The results of these analyses are given in Tables 1, 2, 3, and 4. Back-scatter electron images of the Nb-Ti and Nb-Ti-Ta rods are shown in Figs. 5 and 6, while a cross-section of the Nb-Ti-Ta composite is shown in Fig. 7. A striking feature of the back-

Table 1: Chemical Analysis of a Nb-Ti Rod.

Analysis*	Ti wt.%	Nb wt.%
1	46.2	50.8
2	50.4	49.6
3	50.0	50.0
4	46.3	53.7
5	46.5	53.5
6	45.9	54.1
7	44.3	55.7
8	44.4	55.7
9	44.3	55.7
10	43.8	56.3
11	41.8	58.2
12	41.4	58.6
13	41.1	58.9
14	41.1	58.8
15	47.3	52.7
16	45.8	54.2

*Analysis points ~ 10 μm apart.

Table 2: Chemical Analysis of a Nb-Ti-Ta Rod

Analysis*	Nb wt%	Ti wt%	Ta wt%	Area
1	31.9	39.8	28.5	Light
2	32.3	42.4	25.8	Average
3	32.6	48.3	19.1	Dark
4	33.0	37.3	29.7	Light
5	32.6	47.3	20.2	Dark
6	32.0	39.9	28.3	Average
7	32.0	47.4	20.5	Dark
8	32.5	41.5	26.1	Light

*Analyses were carried out in areas showing maximum light or dark contrast in the back-scattered image.

Table 3: Chemical Analysis of a Nb-Ti Composite

Filament	Nb wt%	Ti wt%
1	54.3	45.8
2	54.3	45.7
3	54.5	45.6
4	54.4	45.5
5	53.7	44.9
6	54.3	45.6
7	53.8	46.2
8	54.7	45.3
9	54.0	46.0
10	54.0	46.0
11	53.9	46.1

Table 4: Chemical Analysis of a Nb-Ti-Ta Composite

Filament	Nb wt%	Ti wt%	Ta wt%
1	34.4	40.0	25.7
2	31.9	41.1	27.0
3	32.7	40.3	27.2
4	31.5	41.4	27.1
5	32.2	42.6	25.3
6	33.4	41.1	25.6
7	31.8	42.5	25.8
8	32.3	45.8	22.1
9	31.5	44.6	24.0
10	31.1	46.1	22.9
11	31.3	46.0	22.7
12	31.9	45.2	22.9
13	32.6	41.4	26.0
14	33.1	41.5	25.4
15	30.3	41.8	27.9
16	32.4	45.6	22.0
17	32.1	43.2	24.7

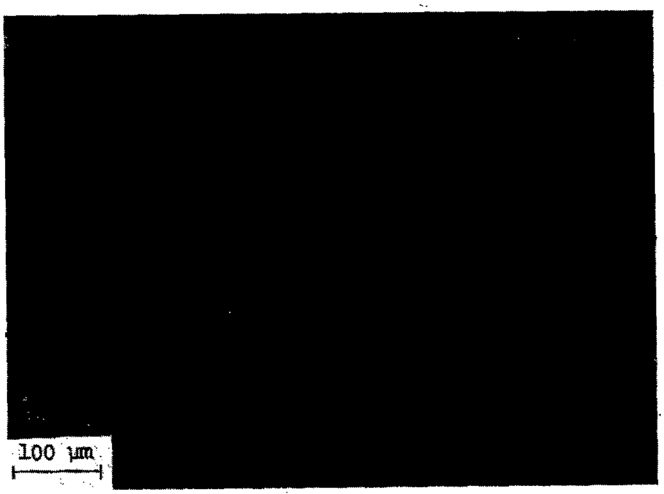

Fig. 5. Nb-Ti rod, unhomogenized. Back-scatter electron image.

scatter images is the pronounced banding resulting from local coring. The scale of the coring is about 10 µm in both cases. The folded nature of the banding results from the swaging steps in the rod reduction process. The EDX spot analyses show that both rods had large local composition gradients, the Ti content ranging from 41.1 to 50.4 wt.% in the binary alloy. The ternary alloy showed little variation in Nb content (31.9 to 33.0 wt.%) but there was a large variation in Ti (39.8 to 48.3 wt.%) and Ta content

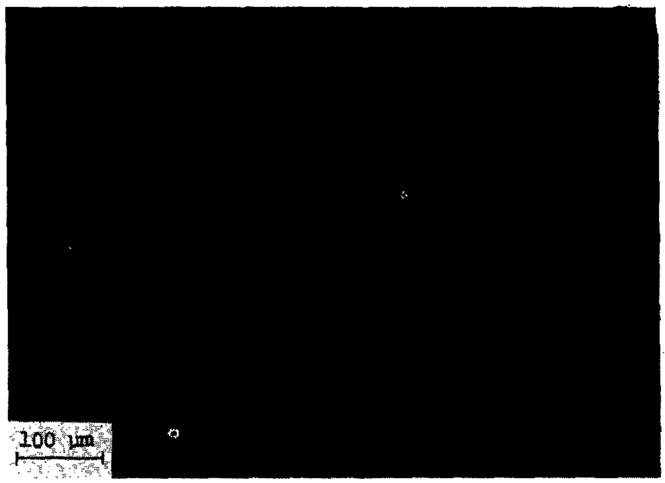

Fig. 6. Nb-Ti-Ta rod, unhomogenized. Back-scatter electron image.

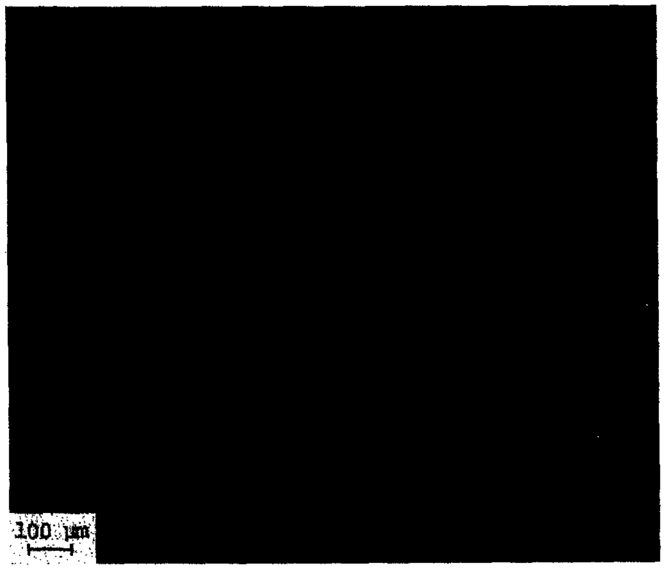

Fig. 7. Nb-Ti-Ta composite. Optical micrograph.

(19.1 to 28.5 wt.%). The cross-section of the Nb-Ti-Ta composite showed many markedly sausaged filaments, in contrast to that of the Nb-Ti composite, which had uniform filaments. Analysis of random filaments in the Nb-Ti-Ta composite showed almost as large a composition variation as the alloy rod; the Ta content varied from 22.0 to 27.2 wt.%, the Ti from 40.3 to 46.1 wt.% and the Nb from 30.3 to 33.4 wt.%. By contrast, the variation found in the binary composite was only 1.2 wt.%, which is on the order of the experimental uncertainty.

III. Homogenization Heat Treatments

Coring can be removed by a homogenization heat treatment; we have normally used a treatment of 8 hrs at 1300 - 1350°C on our laboratory scale arc melted alloys. Such high temperatures are needed because of the high melting point of Nb-Ti. Such high temperatures are experimentally inconvenient and are also high enough to give concern about contamination of the material by atmospheric gases. Determination of the correct anneal requires a decision on the scale and degree to which homogenization is required, as well as a knowledge of the scale of the original coring and the appropriate diffusion coefficients. The scale of the microstructure determining J_c is 5 - 50 nm and the crucial α-Ti precipitation process requires uniform composition and sub-band structure at a size of about 50 nm. However, experimental determination of the degree of homogenization on this fine a scale is difficult. The conventional tool used is the SEM or electron probe with a spatial resolution limit of ~ 1 - 2 µm and a chemical resolution limit of ~ 1%. The back-scatter electron images seen in Figs. 1 and 2 have a greater spatial resolution (~ 0.1 - 0.2 µm) but are only qualitative. Back-scatter images can normally detect atomic number variations of ~ 1, which corresponds to a Ti content variation of ~ 5% for a Nb 50 wt.% Ti alloy. Thus these tools can be applied to the ingot or rod at large size but they become progressively less useful as the rod is reduced to a fine filament in the composite.

To provide additional input to this problem, we have attempted a theoretical calculation of the time and temperature needed to remove coring. The calculations use the analytical approximations of Unman et al.[8] For this calculation it was necessary to make three approximations; one that the rate of homogenization was governed by the diffusion of Nb in Nb-Ti; two, that the initial dendrites were pure Nb or pure Ti; and three, that the Nb-rich dendrite arms had a particular radius. Measurements from 30g ingots melted in our laboratory yielded a value of approximately 10 µm for the dendrite arm radius in a Nb-50 at% Ti, (Nb-34 wt.% Ti), alloy. The dendrites in a large 0.5 m dia ingot have been shown to be ~ 100 µm in width[2] but fabrication of the ingot will rapidly reduce this size. Values of the diffusion coefficient for Nb were taken from our own data.[9] Using these values, it was possible to calculate the length of time required to reduce the difference in composition between the dendrites and the average overall alloy composition to values between 5 and 0.01 at %. These calculations were carried out for heat-treatment temperatures of 1300 and 1400°C over the whole range of alloy compositions from 0 to 100 at % Nb, and are plotted in Figs. 8 and 9. As an example, for a homogenization temperature of 1300°C, the composition of the dendrites in a Ti-44 at% Nb, (Nb 39.6 wt.% Ti) alloy would be within 0.01 at% of the average alloy composition after an 8 hour heat-treatment.

Figs. 8 and 9 show that homogenization can in all cases be achieved for heat treatments of less than 50 hours at 1400°C. In fact the actual times required are likely to be shorter, since the assumptions that the effective diffusion coefficient is that of Nb and that the dendrites are initially either pure Nb or Ti are both pessimistic ones.

IV. Discussion

The results of the present paper are interesting from a number of points of view. We have previously emphasized that what is required for the development of the highest J_c values is an ordered heterogeneous microstructure on a scale of less than about 40 nm.[12] A companion paper[10] shows details of the microstructure of such high J_c composites and confirms that a common feature of all the high J_c (> 2000 A/mm^2 5T, 4.2K) composites that we have studied is the presence of dense walls of α-Ti with average separations of ~ 30 nm. These dense arrays can only be formed when the initial sub-band structure is as regular as possible,

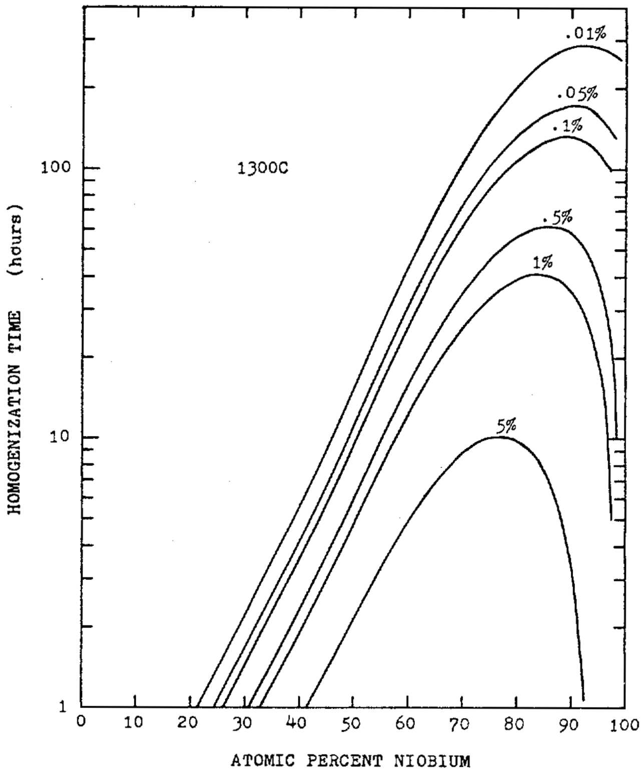

Fig. 8. Calculated homogenization treatment, 1300°C.

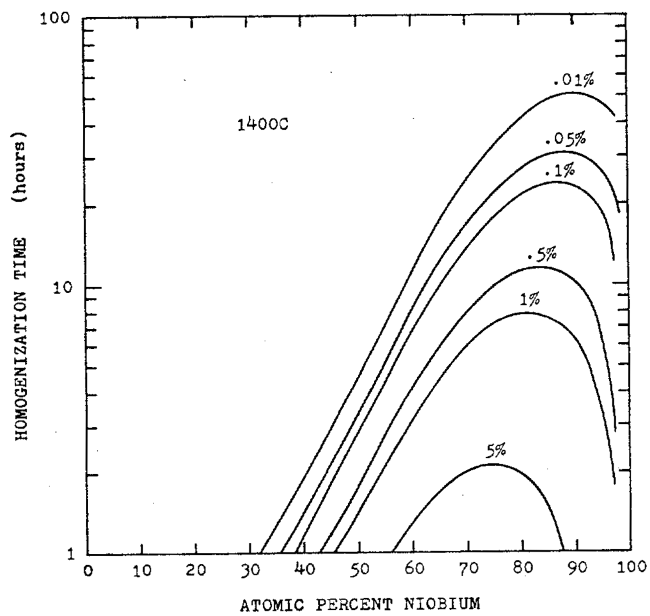

Fig. 9. Calculated homogenization treatment, 1400°C.

since the nucleation and growth of α-Ti occurs preferentially in the sub-band walls.

In contrast to the desired regular state just described, the present results provide evidence for both chemical and structural inhomogeneities in single phase alloys and show that a chemically and structurally irregular microstructure produces an irregular α-Ti distribution after heat treatment (Figs. 3 and 4). One example of gross coring at the large rod size was found to be associated with filament sausaging at final composite size. We now explore these findings in more detail with a view to assessing the general effect of chemical inhomogeneities in Nb-Ti and its alloys.

The most obvious effects were seen in the Nb 43 wt.% Ti 25 wt.% Ta alloy. This ingot was melted at about 150 mm diameter and first examined by us at about 19 mm, when inverse segregation of Ti and Ta to the extent of about 10 wt.% was found to be present. This chemical inhomogeneity was also found in random checks of the sausaged filaments shown in Fig. 7. Although it cannot be proved that the sausaging was provoked by the chemical segregation, it is certainly a reasonable supposition. The elastic modulus of the group IV - V alloys is well known to be very sensitive to the local electron to atom ratio and the inverse segregation of Ti and Ta found here is likely to be much more deleterious to the properties than that of the iso-electronic Nb and Ta. It should also be noted that excessive α-Ti precipitation was also suggested as a reason for the sausaging of this billet.[11] Irregular, localized precipitation in the Ti-rich regions would be an obvious consequence of the observed inhomogeneities, although the form of the flux pinning curve observed for this composite suggested too little, rather than too much α-Ti precipitation.[12]

A more general aspect of the problem is suggested by the results on the binary Nb 46.5 wt.% Ti rod where the inhomogeneities had a similar scale and magnitude. The irregularity of the microstructures even after considerable cold-work is very surprising. For example, our studies of a Fermilab composite[7,10] have shown that a cold area reduction of 300:1 produces a reasonably regular sub-band structure, of average diameter 69 nm. Although some sub-bands were aspected, they did not show the large aspect ratio of those shown in Fig. 3, where a markedly irregular structure is shown. The cold area reduction of the present case is almost identical, being 313:1. It is tempting to associate some of the sub-band bending seen in Fig. 3 with the grosser folding produced by sausaging (Fig. 6) but further tests must be made before we can be certain on this point. Based on our understanding of the microstructures of high J_c composites, however, we would not expect that rods with these inhomogeneities would be an appropriate choice for such a composite.

A question which naturally arises is the extent to which the results presented here are typical. However, our results are too few in number to provide any firm answer. It is not surprising that initial melts of a new ternary alloy would have shown some inhomogeneity. Ta has a high melting point and there are a number of experimental variables in consumable arc melting which can affect the ingot homogeneity. The Nb-Ti result was more surprising but it may be noteworthy that our filament analyses on a randomly selected composite did not show the effect. We have recently analyzed further ingots of Nb 41 wt.% Ti 15 wt.% Ta and Nb 46.5 wt.% Ti made by Wah Chang. The segregation was much reduced in both ingots, being undetectable in the binary alloy and of order about 2 wt.% in the ternary. It thus appears perfectly feasible to control the problem on an industrial scale and specially prepared homogeneous material is now available for special order.[13] In view of the microstructural observations described in this paper, we believe that selection of homogeneous starting material will be fully justified by the gains in J_c arising from a more uniform microstructure.

Acknowledgements

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