

DEVELOPMENT OF IN SITU SECOND PHASE PINNING STRUCTURE IN NIOBIUM-TITANIUM BASED SUPERCONDUCTING ALLOYS

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Abstract

A niobium-based superconducting alloy has been developed which has a rare earth second phase that segregates between the matrix dendrites during solidification. The second phase can be refined by conventional deformation without heat treatment so as to form an in situ fiber network. In such an alloy, one has independent control of the second phase volume fraction as well as the matrix composition. The development of the in situ alloy along with early microstructural and critical current results on the first wires are reported.

Introduction

Superconductors can carry high current densities (J_c) in high magnetic fields when they contain regions of different superconducting properties from the matrix. These regions pin the magnetic field and thereby allow a macroscopic transport current density (J_{ct}) to flow. Conventionally, niobium-titanium alloys (Nb-Ti) are thermally and mechanically processed to produce a titanium-rich second phase within the matrix. This second phase has a ribbon morphology of thickness and spacing (1-10nm) similar to the magnetic field flux line lattice (FLL) in the superconductor.¹ The second phase can strongly pin the FLL, resulting in high J_{ct} desirable for commercial applications.

For various stability reasons, applications require that such superconductors be subdivided into filaments of diameter typically 5-50 microns. Conventional processing consists of casing a billet of Nb-Ti with copper and mechanically working the billet into a monofilament wire. Deformation that reduces the alloy cross section and simultaneously increases its length is quantified by strain. The true strain ϵ is represented by $\epsilon = 2\ln(d_0/d)$, where d_0 and d are the initial and final wire diameters, respectively. The monofilament wire is sectioned into lengths and restacked into another copper can. This can is thermally and mechanically worked through extrusion and drawing with periodic isothermal heat treatments, resulting in a multifilament Nb-Ti superconductor wire.² The heat treatments are performed at specific times, temperatures, and strains for the filaments to give the desired second phase FLL pinning morphology. Size limitations constrain the available deformation true strain to approximately 12 (approximately 18 if the strain before extrusion is considered).

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The heat treatments necessary for the titanium second phase precipitation soften the copper matrix and somewhat harden the Nb-Ti. Unfortunately, the differential hardness between the Nb-Ti filaments and the copper matrix can lead to instability on further drawing. Copper forms brittle intermetallic nodules at the Cu/Nb-Ti interface at heat treatment temperatures,^{3,4,5} which also leads to filament instability. Instead of maintaining a cylindrical shape during subsequent deformation, the filaments "sausage" whereby periodic necked regions form along the filament length. J_{ct} is limited by the narrowest cross section in the filament.⁶ Thus it is desirable to be able to avoid heat treatment for instability reasons as well as the obvious costs of heat treatment time, capital, and labor. Elimination of the heat treatments require other methods of creating second phase networks to pin the FLL.

Zeitlin et. al⁷ produced a two phase network of artificial centers by stacking Nb-Ti rods into Nb tubes. Unfortunately, a true strain of about 30 is required since the Nb tubes must be reduced from a few millimeters wall thickness to a FLL dimension.

This paper considers an alloy which has 10-40 volume percent of second phase pinning structure that is formed during normal solidification.⁸ The alloy can be Nb-Ti or possibly a ternary or higher alloy using for example Ta or Zr which are chemically similar to Nb and Ti, respectively. The second phase is a ductile rare earth metal or metals soluble in the alloy melt but virtually insoluble in the solid state. Thus the rare earth and titanium content of the alloy control the volume fraction of the second phase and the matrix composition, respectively. The second phase can be reduced to the size of the FLL within the drawing strain available in conventional processing. Therefore, the need for conventional heat treatments is eliminated.

Development of the Alloy

In the past ten years, binary alloys of superconducting interest in which the elements are insoluble in the solid state have been studied. Bevk et. al⁹ studied a copper 18.2 vol.% niobium alloy. In this material, niobium dendrites which were a few microns in size after solidification elongated into a very fine filamentary network on the scale of 10-100nm after extensive deformation. This material was named an *in situ* alloy since the filaments formed naturally during the processing. Not only does this material possess high strength from the fine filament array, but the insolubility of niobium is so complete that the copper retains a high

conductivity.

An analogous process is developed here for forming an in situ composite material. A conventional superconductor (principally Nb-Ti, possibly containing Ta, Zr, or Hf) matrix is made containing an insoluble metal or metals "M". The material "M" will segregate between the Nb-Ti dendrites on solidification and form a fibrous network in the Nb-Ti matrix during conventional conductor processing. The fibers will be analogous to the flux pinning α -titanium ribbon precipitates in conventional Nb-Ti conductors and thus "M" will be of the proper spacing and thickness to be effective for pinning the flux line lattice.

A list of criteria for such a material "M" to meet can be made for such an in situ pinning center material (consider a Nb-Ti matrix at present):

- 1). Should be ductile enough to form a filamentary structure by conventional wire drawing (ie. "M" should be a metal to possess the desired ductility).
- 2). Should not form a compound with Nb or Ti.
- 3). Should not be soluble in Nb or Ti to the extent of degrading the superconducting properties of the Nb-Ti matrix.
- 4). Should be miscible in the melt to avoid segregation.
- 5). Should have a hardness similar to the matrix for uniform fiber formation during deformation.
- 6). Should not have a melting point too different from the matrix (approximately 1900°C for Nb-Ti) to prevent macrosegregation and allow easier processing.
- 7). Should have a low vapor pressure at the melting point to avoid melting difficulties.
- 8). Additional cost of the alloy Nb-Ti plus "M" should not exceed the saved cost of heat treatment capital, labor, and time.

A detailed search of the periodic table for a material "M" has been made. Binary phase diagrams between potential element(s) M and either niobium or titanium were surveyed¹⁰⁻¹³. The periodic table can be subdivided according to crystal structure. Elements with a body-centered-cubic (BCC) structure, for example vanadium, chromium, iron, molybdenum, tantalum, and tungsten are either soluble in or form intermetallic compounds with niobium, which is also BCC. Lithium and sodium do not form compounds with niobium or titanium, but both have very low melting points and high vapor pressures.

The face-centered-cubic (FCC) elements aluminum, nickel, copper, palladium, platinum, gold, and lead all form titanium compounds. Rhodium and iridium form intermetallic compounds with niobium. Calcium forms no compounds with either niobium or titanium, but its melting point is low and vapor pressure is high. Silver forms titanium intermetallic compounds below 1020°C which would be likely to form during extrusion processes if not during solidification. Cerium forms no titanium compounds, but has a strong immiscibility with niobium. The melting point of cerium is more than 1000°C lower than NbTi and thus may make processing difficult.

Metals with a hexagonal close packed (HCP) structure are generally not as ductile

as FCC or BCC metals, but microstructural evidence from NbTi alloys show that Ti second phase on the order of 0.5 micron in size is ductile enough to form fine ribbons suitable to pin the FLL^{1,14,15}. Since the in situ formed metal "M" will be dispersed into regions a few microns in size, the HCP metals are worthy of consideration.

Magnesium is quite immiscible with niobium and has a low melting point of 650°C. Beryllium, cobalt, rhenium, and osmium form compounds with niobium. Zinc forms intermetallic compounds with titanium. Ruthenium forms a solid solution with niobium. Zirconium and hafnium form solid solutions with titanium. Exhausting virtually all of the transition elements leads one to consider the rare earth elements.

The rare earths (except for cerium already mentioned and BCC europium, which has a low melting point) are HCP and show immiscibility with niobium to different extents and do not alloy with titanium. All are candidates for the in situ metal "M". However, the light rare earth elements, atomic numbers 57 through 63, all have a melting point below 1075°C, making processing difficult.

Nearly all of the remaining heavy rare earth elements, atomic numbers 64 through 71, as well as scandium, atomic number 21, and yttrium, atomic number 39, have a melting point above 1300°C (ytterbium is an exception). The niobium immiscibility does not occur over as large of a range of composition as with the light rare earths. The vapor pressure of dysprosium, holmium, erbium, thulium, ytterbium, and scandium are quite high, making melting of these metals difficult. Thus the elements yttrium (Y), gadolinium (Gd), terbium (Tb), and lutetium (Lu) appear to be the best choices for "M". Gd and especially Tb and Lu have a strong cost disadvantage to yttrium. These elements have a similar molar volumes; however the lower atomic number of yttrium makes it cheaper on a cost per unit volume of second phase basis. Gd is ferromagnetic and may justify its higher cost if ferromagnetism in the in situ second phase is helpful at pinning the FLL. Ito et al.¹⁶ show that 30 atomic percent or more of Y can be added to Gd without loss of low temperature ferromagnetism. A Y and Gd mixture may be a cost saving compromise should Gd prove to be a preferable in situ addition. Finally we note that Zr can replace Ti in the above analysis with identical results.

Experimental

Commercial Nb-46.5 wt.%Ti (Nb-63 at.%Ti) is processed and heat treated so as to produce about 20-25 vol.% α -Ti precipitate in its optimum state.^{14,15} In this state, the matrix composition is about 49 at.% titanium. A test alloy (in atomic percent) of 35Nb-50Ti-15Y was made. This composition yields 24 vol.% percent yttrium second phase in a Nb-Ti matrix of 61 at.% titanium. Gd has the same atomic volume as Y, therefore comparable Gd alloys would have the same at.% rare earth as yttrium containing alloys.

99.9% pure Nb, Ti, and Y were surface cleaned and weighed out in correct amounts to

give a 35Nb-50Ti-15Y alloy of total weight of about 30 grams. The metals were melted in a laboratory arc-melter under 250 Torr of high purity argon. The chamber was oxygen gettered by melting a pure Zr button for several minutes. The metals were melted together as a button several times to ensure homogeneity and finally into a 9mm rod-like shape. A sample from this rod was mounted for light microscopy, microhardness, and Energy Dispersive X-ray (EDX) analysis.

The rod was swaged to about 4mm and placed in a copper tube of 0.635mm (0.25 inch) with a 1.0mm (0.035 inch) wall thickness. The alloy with copper jacket was drawn to a diameter of 0.16mm for a strain of 8.41. Samples were taken at various strains for microhardness and light microscopy. Samples at strains (diameters) of 6.09 (0.51mm), 7.48 (0.25mm), and 8.41 (0.16mm) had their transport critical current density (4.2K) measured in transverse magnetic fields to 10 Tesla.

Results

Figure 1 shows the microstructure of the as-melted alloy rod, indicating a two phase microstructure. EDX analysis was performed on a matrix region, a second phase region, and a 50x50 square micron area covering several matrix and second phase regions. The EDX traces are shown in Figure 2. The lighter matrix area is Nb-Ti with no yttrium detected. The darker second phase is yttrium with about 10 weight percent titanium according to the EDX analysis. This is more than expected according to the binary phase diagram.¹³ It is not clear whether some of the higher energy K α titanium signal emanates from the matrix beneath. The wide area scan in Figure 2 indicates the bulk composition of the 35Nb-50Ti-15Y. The yttrium second phase composes nearly 25 area percent of the micrograph, in agreement with the initial volume percent calculation.

The second phase is dispersed into approximately 2 micron regions about 8 microns apart. Some porosity amongst the yttrium second phase can also be seen in Figure 1.

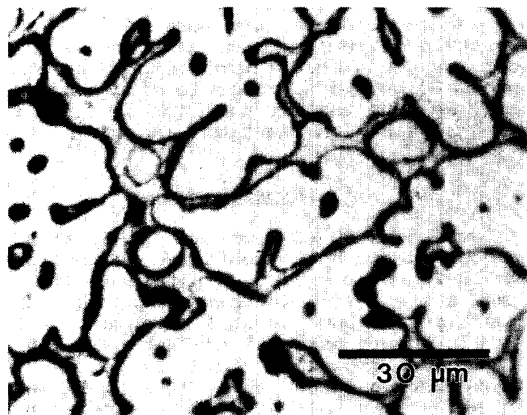


Figure 1. A light micrograph of the as-solidified alloy 35Nb-50Ti-15Y. A two phase structure with about 25 volume percent second phase is seen. Occasional shrinkage porosity can be seen in the second phase.

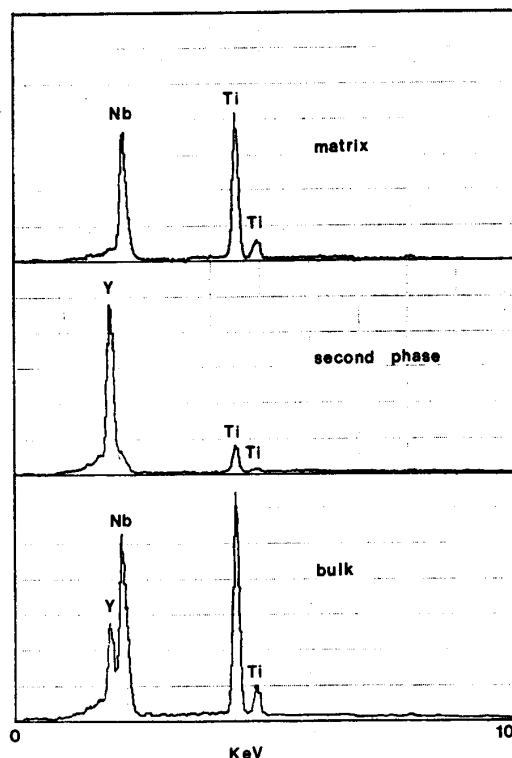


Figure 2. EDX analysis of a matrix area (top), a second phase area (middle), and a 50x50 micron square survey area covering several matrix and second phase regions. The matrix shows only NbTi. The second phase contains largely yttrium with about 10 weight percent titanium.

The Nb-Ti matrix freezes with the liquid yttrium between the dendrites. When the yttrium freezes upon further cooling, the volume change results in porosity. Evidence for the dendritic nature can be seen in the micrograph of Figure 3 taken near the bottom side of the rod where solidification began. Dendritic growth can be seen to grow away from the copper mold.



Figure 3. A micrograph of the as-cast alloy near where the rod first solidifies. The NbTi primary phase is seen to grow away from the mold in the direction of the arrow shown.

Figure 4 shows a transverse section light micrograph after a strain of 3.54. A reduction in the second phase thickness and spacing is seen compared to the unstrained sample in Figure 1. X-ray diffraction indicates the formation of the conventional (110) texture in the BCC matrix as well as a (0110) texture in rare earth second phase, as is typical for HCP metals.

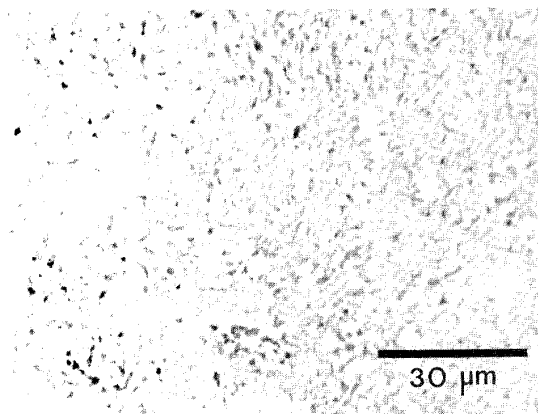


Figure 4. Alloy of Figure 1 after a true strain of 3.54, transverse section. The yttrium thickness and spacing have been co-reduced with the NbTi matrix.

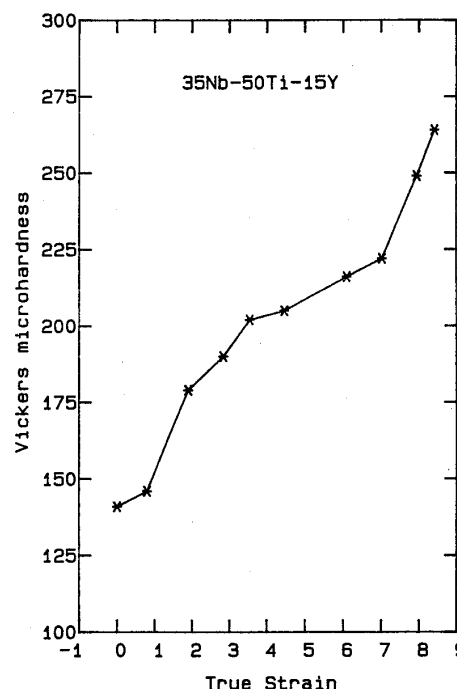


Figure 5. Microhardness vs. strain for the 35Nb-50Ti-15Y alloy.

Microhardness data in Figure 5 show work hardening with an almost linear increase in hardness with strain. Microhardness indentations span several yttrium second phase and matrix regions. A 141 Vickers microhardness in the as cast condition is comparable to binary Nb-Ti (140-170). The microhardness increases to 264 at a strain of 8.41, where for comparison conventional Nb-Ti has a hardness typically 200-250 in the precipitated 2 phase state.¹⁷

Figure 6 shows J_{ct} for samples at the higher strain values. These samples are far from their optimum strain to get the yttrium size and spacing on order of the FL. Consequently, the J_{ct} vs. field plot is flat, similar to non-heat treated NbTi. J_{ct} increases with strain as the microstructure becomes finer. It is important to note that the J_{ct} is non-zero beyond 10 tesla. Such a result is a good indication that the superconducting properties of the matrix have not been degraded by the presence of the yttrium. Larger scale experiments are needed to test the superconducting properties of the yttrium at the optimum size and spacing.

The lack of severe work hardening along with indications of co-deformation of the yttrium with the NbTi matrix is encouraging for the in situ material. However, piece length in drawing was poor above a strain of about 3.0 (2mm diameter). Wire fractures were always of a ductile cup and cone nature. It is possible that swaging prior to casing in copper may have created folds in the non-uniform shaped rod. Although the oxygen content of the alloy was not measured, questions of the yttrium purity and of oxygen pickup in melting are of importance

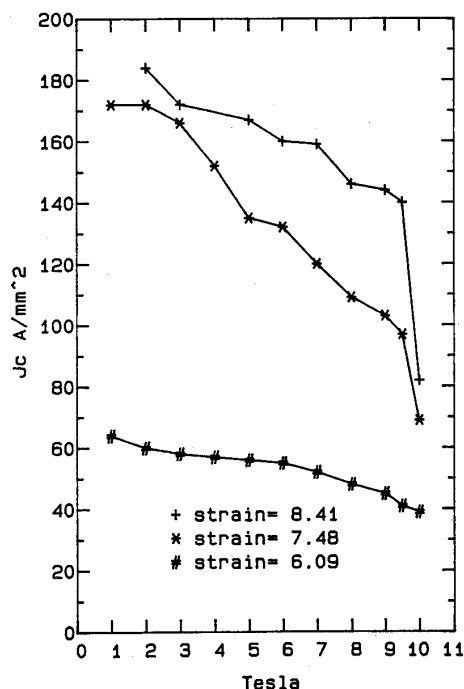


Figure 6. Transport current density (J_{ct}) measurements of the 35Nb-50Ti-15Y alloy as a function of drawing strain. The optimum drawing strain cannot be achieved in this test experiment.

considering the continued work hardening of the alloy at high strains. Figure 7 shows data summarized by Scott¹⁸ on the effect of deformation on the hardness of yttrium of different oxygen contents. It is clear that oxygen content must be minimized.

Discussion

This first experiment clearly demonstrates that the in situ pinning center idea probably is feasible. Rare earth metals can be added to Nb-Ti and therefore to binary or higher alloys containing zirconium and hafnium, to form a ductile, in situ second phase which forms between the matrix dendrites. The rare earth and titanium contents control the second phase volume fraction and matrix composition, respectively. The in situ second phase was found to be about 2 microns thick and 8 microns apart in a conventionally solidified 35Nb-50Ti-15Y alloy. This size and spacing is suitable for producing a FLL pinning morphology in the strain available in conventional conductor processing. The properties of the test alloy have been shown to be satisfactory with respect to easy melting, high ductility and non-degraded superconducting properties.

Although the necessary drawing strain was not physically achievable in this first experiment, the yttrium second phase is shown to co-reduce with the Nb-Ti matrix without severe work hardening. This indicates that it may be possible to achieve the FLL dimension for the rare earth second phase.

Acknowledgement

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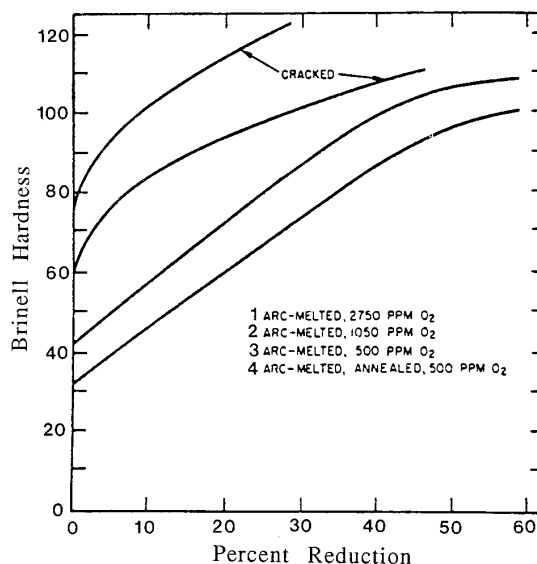


Figure 7. Microhardness vs. cold work for yttrium of different oxygen contents, taken from Scott (ref. 18).