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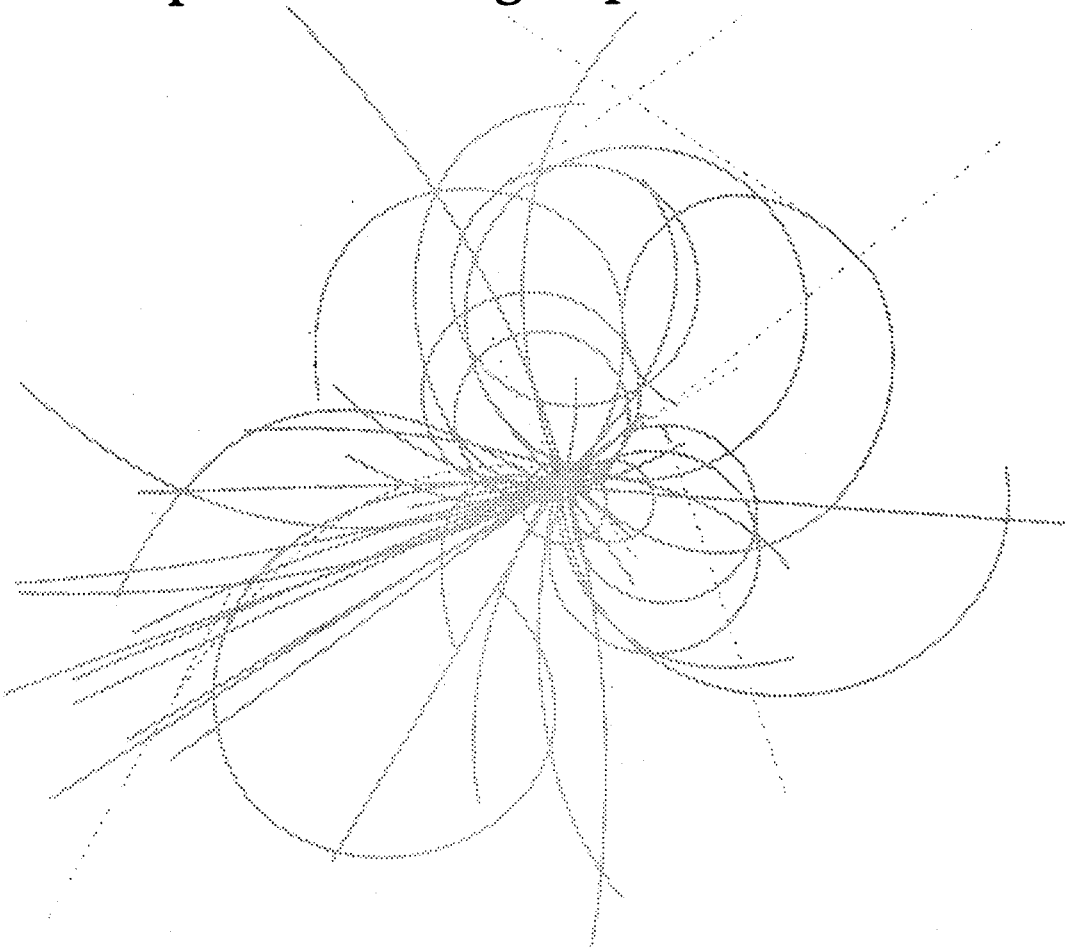

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RAW MATERIALS AND EARLY MONOFILAMENT ANALYSIS FROM THE VENDOR QUALIFICATION PROGRAM

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INTRODUCTION

Eight cable vendors are presently fabricating materials as part of Phase I of the Superconducting Super Collider (SSC) cable qualification program. This program is designed to prepare each vendor to compete for the supply of superconducting cable for dipole and quadrupole magnets for the SSC magnet subcontractors. Phase I is split into a final R&D effort (Phase IA) of approximately 4000 kg, and a baseline production process of 3500 kg (Phase IB). As part of the R&D effort variables for most cable vendors, approximately half of the Phase IA billets are being fabricated using NbTi alloy from the cable vendors' "primary" alloy vendor and the remainder from a "secondary" alloy vendor, as the vendor sees appropriate. All cable vendors have chosen Teledyne Wah Chang-Albany (TWCA) as their primary alloy source. Two cable vendors have chosen Toho Titanium, and four have chosen NRC, Inc., as their secondary alloy source.

The purpose of this paper is to report the typical values quoted on material supplied in this effort as well as verification measurements made at the SSC Laboratory (SSCL). The final product chemistry, grain size, hardness, and radiographs from the alloy vendors will be reported along with grain size, hardness, and relative homogeneity measured by EDX at the SSCL. Normalized monofilament extrusion data are also discussed. Data will be analyzed for significant differences in raw material properties. These differences are to be noted during future analysis of the final strand manufactured from these material. Only at that time will it be possible to determine positive or negative impacts of specific properties of the raw materials.

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EXPERIMENTAL

Chemistry data on raw materials are as reported to SSCL. Specification SSC-Mag-M-4000A for NbTi alloy and specification SSC-Mag-M-4001 for niobium barrier require the submission of data for raw materials. Samples of NbTi alloy supplied to SSCL were either disk samples of ingot or post extruded rod. Samples of Nb sheet were also supplied. Hardness measurements were made with a Leco M-400-G1 micro hardness tester with a 300-g load and a Vickers indentor. Grain size was measured as a function of radius on samples etched with a 1:1:1:1 mixture of hydrofluoric acid, nitric acid, lactic acid, and water, and photographed with a Mitutoyo FS-110 light microscope. The relative homogeneity of the NbTi alloy was measured on as-polished sections using a Link eXL energy dispersive X-ray analysis (EDX) on a JEOL 6100 scanning electron microscope (SEM). An X-ray spectrum collected over an approximately 1-mm^2 area was used as a standard and assumed to be equivalent to the average composition specified by the vendor. Each run consisted of a line along the specimen radius comprised of 101 points spaced 10 μm apart. Two runs were made on each sample, one line near the center of the sample and the other near the outside. Integrated peak height ratios were corrected for atomic number, absorption, and fluorescence (ZAF) in the Link program. Tensile measurements were made using a Instron 4302 Tensile Testing system with flat serrated grips. Transmission radiographs of NbTi disks were made taken by Bonded Inspection, Inc. Image analysis was used to enhance the brightness and contrast to reveal features difficult to detect in a standard image of a X-ray radiograph. Image analysis was performed using the Link eXL system connected to either the SEM or a Hitachi KP-MIU video camera. A complete description of image analysis routines will be published elsewhere.

RESULTS

The heat numbers for the NbTi alloy and Nb sheet used at each of the cable vendors for Phase I were checked for commonality between vendors. One cable vendor has two heats in common with two other cable vendors. No common heats of secondary alloy sources were found among the cable vendors.

Table 1 contains averages for the alloy compositions and hardness, as well as typical ASTM grain size numbers for the heats of the primary and secondary sources for each of the cable vendors. Averages and coefficients of variation (C of V, the standard deviation divided by the mean) are calculated for each alloy vendor's material. Only a subset of the elements listed for analysis in the SSCL specifications is given. Elements required by the specifications (but not listed here) vary little between heats or between alloy vendors.

Table 1. Reported data on NbTi alloy from three alloy vendors.

Cable Vendor	Mean Ti%	Mean O ppm	Mean C ppm	Mean Fe ppm	Mean Si ppm	Mean Ta ppm	Grain Size ASTM	Hardness Hv
1	46.5	550	45	36	25	828	3.7	130
2	46.6	511	39	36	25	893	4.0	129
3	46.7	525	40	42	62	937	3.7	132
4	46.5	581	98	65	100	827	2.0	133
5	46.4	542	74	47	57	884	3.3	133
6	46.7	555	32	44	45	938	2.5	131
7	46.5	603	41	43	44	798	3.2	132
8	46.7	560	40	35	25	905	2.5	128
TWCA ave.	46.6	553	51	44	48	876		131
C of V (%)	0.2	5.7	47.1	22.6	53.9	6.4		1.2
	47.6	543	88	60	3	47	4.3	131
	47.7	608	112	85	5	56	6.0	140
	47.8	533	97	63	6	31	5.0	133
	47.4	422	106	45	10	95	5.0	125
NRC ave.	47.6	527	101	63	6	57		132
C of V (%)	0.4	14.7	10.4	26.1	49.1	47.5		4.7
	47.5	343	40	116	20	696	6.3	127
	47.7	346	102	107	53	777	2.5	126
TOHO ave.	47.6	345	71	112	37	737		127
C of V (%)	0.3	0.6	61.7	5.7	63.9	7.8		0.6

Table 2 contains select reported Nb chemistry data as well as yield strength and elongation for the four Nb sheet vendors used by the cable vendors. The number of heats is too small to calculate C of V for each vendor. Table 3 contains an average and range of the reported copper RRR for can materials of each cable vendor.

Table 2. Reported data on Nb sheet sorted by Nb sheet vendor.

Nb Vendor	Mean O ppm	Mean C ppm	Mean Fe ppm	Mean Si ppm	Mean Ta ppm	Grain Size	Yield MPa	Elongation Percent
Cabot	200	20	10	10	140	8.0	98	40
NRC	81	11	20	20	200	6.1	92	31
DENKAI	80	40	10	20	900	4.0	81	24
TWCA	65	25	50	40	690	8.0	108	46

Table 3. Reported copper RRR values for monofilament and multifilament cans.

Vendor	Min RRR	Max RRR	Average	C of V Percent
1	345	404	384	4
2	148	301	183	16
3	301	358	336	9
4	317	346	328	4
5	269	317	285	7
6				
7	317	343	322	4
8	282	288	286	1

Table 4 shows selected homogeneity, hardness, and grain size data measured at the SSCL from each of the alloy and sheet vendors. The reported hardness and grain size from the alloy and sheet vendors are given for comparison. The samples chosen reflect the range of diameter and heat treat conditions supplied by each cable vendor.

Figure 1 shows relative titanium concentrations along 1-mm-long radial lines for the same samples from each alloy vendor as in Table 4. The radial line was approximately 1 cm from the surface of each disk, and the standard deviation for each data set is given in Table 4.

Table 4. Homogeneity, hardness, and grain size data on NbTi alloy and Nb sheet.

Alloy Sample	Reported wt.% Ti	Measured Std. Dev. Homogeneity	Reported ASTM Major Grain Size	Measured ASTM Grain Size	Reported Hardness Hv	Measured Hardness Hv
NRC 200	47.6	0.40	3	3.5	141	134
TOHO 200	48	0.42	2.5	4.5	124	134
TWCA 200	46.9	0.58	_	3.5	130	140
NRC 250	47.4	0.85	2.5	3.2	144	135
NRC 150	47.6	0.87	4	4	138	138
TWCA 150	46.2	0.38	4.5	3	131	138
TOHO 150	46.8	0.71	5.2	6	129	132
Sheet Vendor	**thickness mm**		**Reported Grain size**	**Measured ASTM**	**Ingot Hardness**	**Sheet Hardness**
Cabot	0.6	_	8	8.5	74	83
Denkai	1.5	_	6	4	56	74
NRC	1.4	_	7.2	3.2	_	65
TWCA	0.6	_	8	7.2	46	80
TWCA	1.54	_	8	8.8	56	79

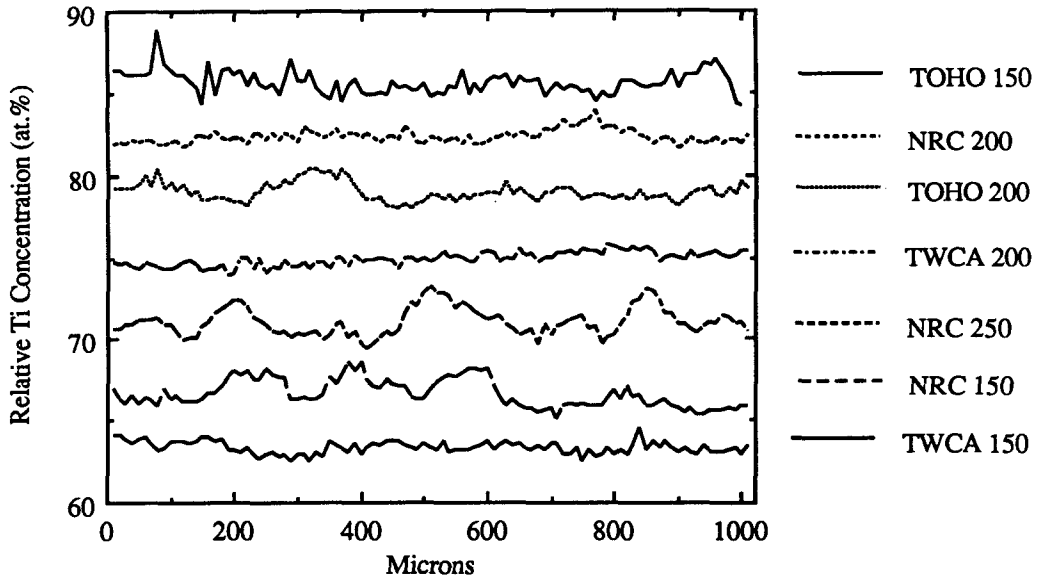

Figure 1. Relative Ti concentrations along 1-mm radial lines in representative material from each alloy vendor. The legend gives the alloy vendor and the material diameter at the time of testing, rounded to the nearest 10 mm.

Figure 2 shows representative micrographs of the grains of each alloy vendor. The NRC grains appear to contain grains and "subgrains". The subgrains are low-angle grain boundaries resulting from the plasma melting process.[1] The subgrain size is the reported grain size in all of NRC data.

Figure 3 shows representative radiographs of each alloy vendor's material. While all raw materials are nominally homogeneous to less than ± 1 %, the images yield some information about the deformation after casting. All alloy vendors' material meets homogeneity requirements, with the exception of one cable vendor's Toho alloy. Some alloy vendors' radiographs were less uniform in brightness than others, which limits the contrast enhancement for the detection of very faint defects.

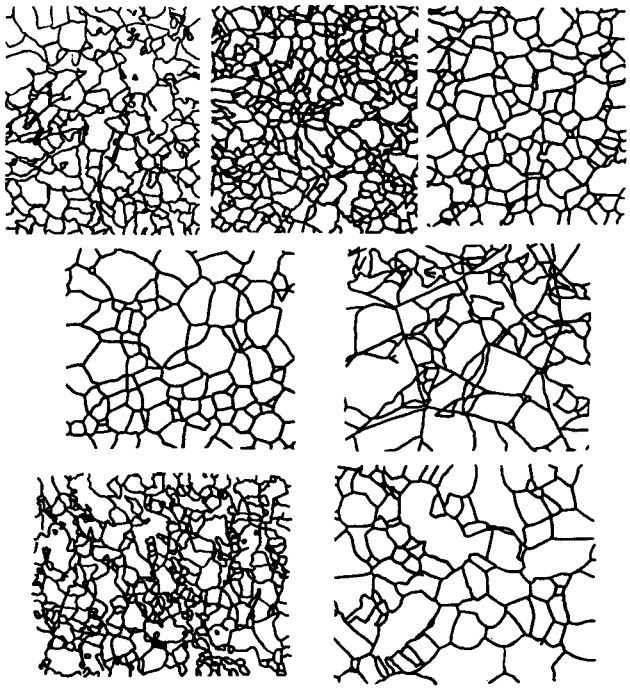

Figure 2. Grain Boundary line traces from nominally 50-X micrographs showing the grains of the samples in Figure 1. From top left to lower right: TOHO 150, NRC 200, TOHO 200, TWCA 200, NRC 250, NRC 150, TWCA 150.

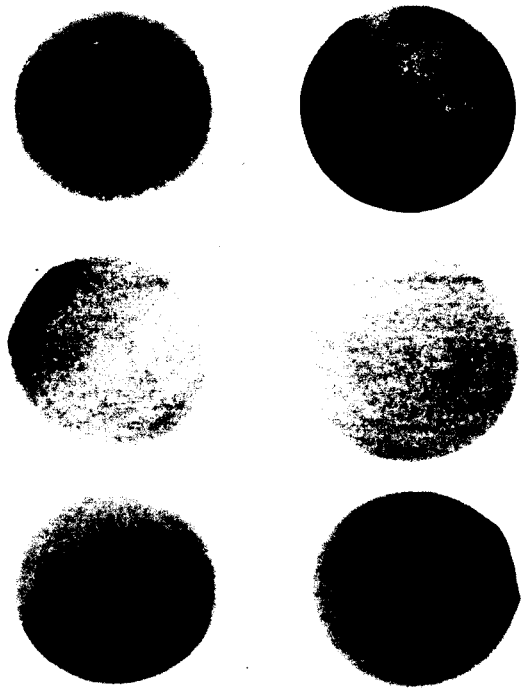

Figure 3. Representative radiographs for each alloy vendor's material. From top left to lower right: TOHO 150, TOHO 200, TWCA 200, NRC 250, NRC 150, and TWCA 150.

Monofilament dimensions, as well as pre-extrusion compaction processes, vary widely among cable vendors. The standard deviations in monofilament diameters, NbTi core lengths, running pressures of monofilament extrusion, and extrusion reduction ratios are 31 mm, 124 mm, 186°C, 183 MPa, and 35, respectively. The area fraction of NbTi at the mid-cross section of the billet at extrusion size has a range of 10%. The SSCL strand specification calls for 1-μm nominal spacings on 6-μm nominal filaments, resulting in a nominal LAR of 0.5 (66 area percent NbTi). The average billet extrusion local area ratio (LAR) for all cable vendors is 0.589. The cross sections of each cable vendor's billets are similar enough to make a comparison of the extrusion data to a modified form of the simple extrusion formula given in Dieter:[2]

$$P' = k \ln (R),$$

where R is the area reduction ratio of the extrusion and P' is the pressure on the front of the extrusion ram. Figure 4 contains a plot of k vs. temperature. Six of the eight vendors were used to form the curve. The other two vendors' processes apparently do not ensure a uniform billet temperature from a billet surface temperature measurement.

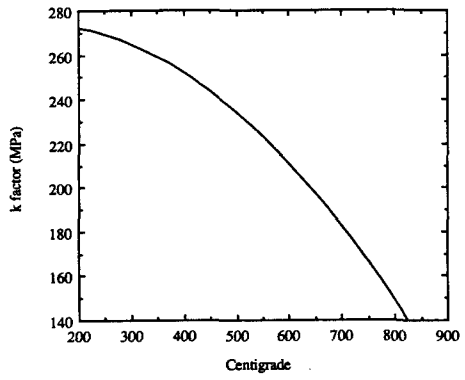

Figure 4. Curve representing k factor vs. temperature data for Phase IB monofilament.

DISCUSSION

Table 2 shows significant differences in the chemistry (wt. % Ti and ppm weight for trace elements) between alloy sources as well as variations in the material from one alloy vendor at different cable vendors. The average titanium concentration of TWCA material is reported at 46.6 wt.%, while Toho and NRC are 1% higher at 47.6 wt.%. Average oxygen contents are considerably lower for Toho alloy (345 ppm wt.) than for TWCA (553) or NRC (527). The average oxygen content of NRC material varies significantly between cable vendors, from a low of 422 to a high of 608 ppm wt. The higher NRC heat numbers tend to have lower oxygen contents than lower NRC heat numbers. The average silicon content of NRC alloy (6) is considerably lower than Toho (37) or TWCA (48). Similarly, the average Ta content is lower for NRC (57) than for Toho (737) or TWCA (876). The hardness for all alloy material is similar at approximately 130 Hv. The grain size for NRC material is finer than either TWCA or Toho of similar billet size. Monofilament billet size differences do not allow direct comparison across all billets.

The average copper RRR varies significantly between cable vendors over a range of 183 to 384. However, the coefficient of variation at each cable vendor is typically a few percent. This translates into a low temperature resistance variation of a factor of 2. Variations in RRR are important in checking for correlations to strand-to-strand contact resistance in finished cables.

The chemical homogeneity data in Table 4 indicate that all alloy vendors' material has a standard deviation of 1% or less. The hardness data for the alloy agree reasonably well with the alloy vendor (overall average of 136 Hv). The measured sheet hardness is considerably higher than the reported ingot hardness, but are quite similar for all vendors (average of 76 Hv). All of the sheet material had equiaxed grains with the exception of NRC sheet, which had an aspect ratio of approximately 4. The circle template method used for grain size measurement (ASTM standard E112–85) averaged the dimensions in the rolling and transverse directions.

Figure 1 shows that all alloy material show some composition variations on a spacing of 200–300 μm. The grain size of X-ray negative film is in the range of 40–80 μm, and therefore this chemical inhomogeneity is on a scale at the limits of X-ray negative resolution. The X-ray negatives in Figure 3 do show compositional variations over a larger scale. The "tree-ring" nature has a size scale on the order of 10 mm. In the case of Toho alloy, Ti freckles are clearly visible from about 0.2 to 0.8 of the sample radius in one cable vendor's material, while the other cable vendor's material supplied by Toho has no freckles and only traces of tree rings. In general, the tree ring nature is less prevalent in TWCA material than in NRC material. However, some heats of both TWCA and NRC material show no tree rings, while others' heats show some tree rings. Tree rings tend to be most prevelant at about 0.75 of the material radius. In some NRC material, the tree rings have a four-fold symmetry. Since cooling on solidification is radial, a square-like tree-ring pattern is thought to result from nonuniform metal working during deformation after casting. Correlations to the NbTi core uniformity in monofilament at restack size will be studied in later work.

Tree rings represent a variation in the Ti content on the order of 1% over a distance of a few hundred microns. Such a variation will affect the Ti precipitation kinetics locally to some extent. The SSCL has observed severely tree-ringed alloy material in past work. In that case, filament distortion (non-roundness), filament roughness (non-smoothness of the NbTi/Nb or Nb/Cu interface), or sausaging (axially varying cross-sectional area) was found not to be significantly worse than other composites. Analysis of monofilament quality is ongoing. Early reports of monofilaments with non-round cores have been reported for *all* alloy vendors' materials. Future work by SSCL will check for correlations to features in X-ray negatives with the monofilament morphologies.

The k factor data in Figure 4 cover a temperature range of nearly 600°C, and ram speeds of 0.3–4 cm per second. Because the correlation coefficient to this curve was 0.98, variations in press design, die design, and ram speed apparently do not strongly affect the k factor for TWCA Phase IB alloy. The data available from the Phase IA billets made from secondary alloy sources show that NRC and Toho alloys have k factors similar to TWCA alloy.

It is likely that the higher titanium content materials from NRC and Toho in Phase 1A will respond differently (both electrically and mechanically) to heat treatments than TWCA material in each cable vendor's baseline process. While it is clear that the alloys from NRC, Toho, and TWCA are significantly different, there are no strong drawbacks at this early stage to using any of these alloys for 6-μm strand fabrication.

ACKNOWLEDGEMENTS

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