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Characterization of U-6Nb Ingots Produced via the Electron Beam Cold Hearth Refining Process

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Report on FY-97 Process Development Program Activity

Abstract

A study was undertaken at Lawrence Livermore National Laboratory to characterize uranium, 6% niobium ingots produced via electron beam melting, hearth refining and continuous casting and to compare this material with conventional VIM/skull melt/VAR material. Samples of both the ingot and feed material were analyzed for niobium and trace metallic elements, carbon, oxygen and nitrogen. This material was also inspected metallographically and via microprobe analysis.

Introduction

Since the mid 1940's, uranium metal has been fabricated into a wide variety of parts at the Department of Energy's Y-12 complex in Oak Ridge, Tennessee. In the case of the uranium-6% niobium alloy, the reactivity of this material in the liquid state results in large amounts of non-recyclable scrap and waste being generated during production. Approximately half of this waste is a direct result of producing the alloy and the remaining half results from thermo-mechanical component fabrication processes. The low yield of the current multi-step flow sheet creates substantial environmental, safety and health liabilities and high cost in the production of these parts.

By use of Electron Beam Cold Hearth Refining (EBCHR), about 80% of the uranium waste generated under current manufacturing methods can be eliminated. Figure 1 demonstrates how a single EBCHR melt can be used to replace eight of the current Y-12 processing steps for the U-6Nb alloy. In addition, the ability to recycle materials stockpiled from current manufacturing processes could reduce the requirement for virgin feedstock to zero for the foreseeable future by working down existing stores of scrap. As an added benefit, it is estimated that this will also reduce radiation exposure levels to plant workers by about 30%.

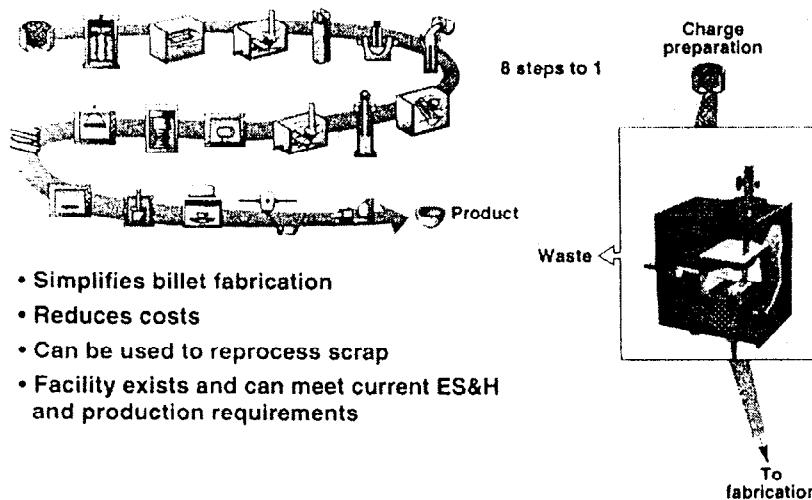


Figure 1: A single electron beam melt replaces eight of the current steps

Current Status

In 1993, LLNL retrofitted an existing, on-site, uranium-qualified vacuum processing system as an EBCHR furnace. In 1994, funding was obtained to demonstrate the capability of producing 5.5-inch-diameter U-6 Nb ingots meeting Y-12 specifications and to design and construct a scrap feeder capable of recycling chopped Y-12 plate scrap [1]. A modeling effort was also initiated to better understand the relationships between input process parameters and final ingot structure.

This facility, shown in Figure 2, is complete and has produced U-6 Nb from both virgin and scrap feedstock which meet Y-12 specifications. In 1996, the furnace was modified to allow the production of 8.25-inch diameter ingots which are necessary to meet the requirements of the current Y-12 production flowsheet. Figure 3 shows both the 5.5" and 8.25" diameter ingot product from this EBCHR furnace.

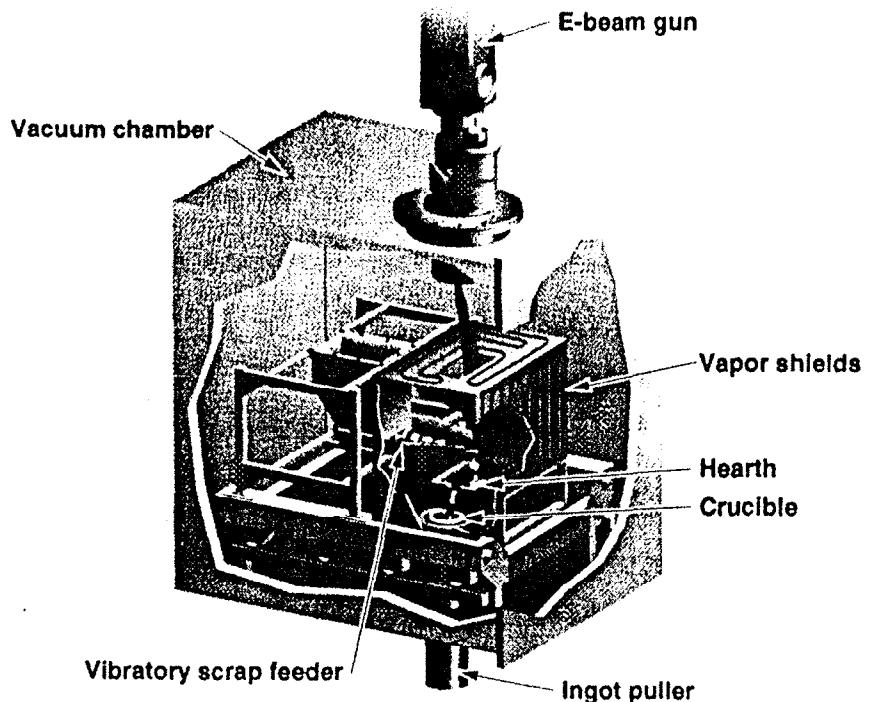


Figure 2: Experimental e-beam casting system at LLNL

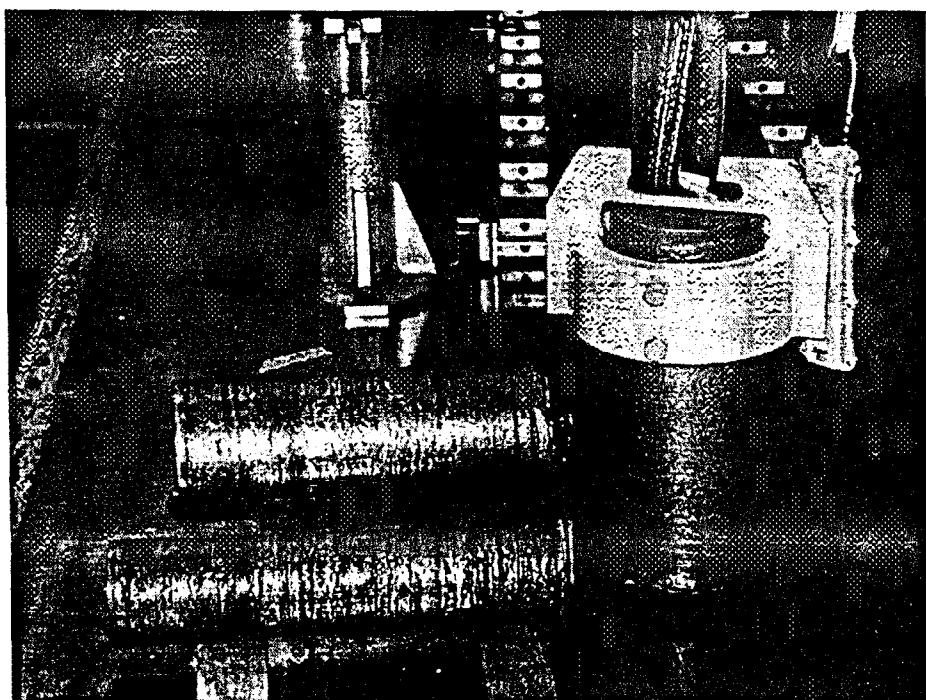


Figure 3: 8.25" and 5.5" diameter U-6Nb ingots

The 1997 effort centered around characterizing the EBCHR produced U-6Nb and comparing it to conventional Vacuum Induction Melted/Skull Melted/Vacuum Arc Remelted (VIM/SM/VAR) material produced at the Y-12 plant. Previous work by Y-12 established the characterization protocol for U-Nb ingots during each stage of the VIM, SM and VAR processing [2] and variations in Nb composition top to bottom and with radial location within the ingot [3]. This current effort attempts to follow these established protocols in characterizing the EBCHR material.

Ingot Production

A full sized 8.25" diameter ingot, 24" long and weighing 315 kg, produced under typical operating conditions was selected for characterization. Raw material for producing this ingot was 100% scrap plate from the Y-12 processing facilities. The plate was nominally .25"- .5" thick and sheared into pieces with a maximum dimension of 3.5" in any direction. The plate was sandblasted at Y-12 to remove loose scale, and was used in the as-received condition at LLNL to produce the ingot. The LLNL EBCHR system utilizes a vibratory feeder to continuously feed this chopped scrap to a refining hearth where it is melted by the electron beam. A light dross forms over the liquid metal in the melt region, presumably from uranium oxides, and possibly silicon oxide from the Y-12 sandblasting, but appears to dissipate in the downstream region of the hearth resulting in a clean, oxide free metal stream being poured from the hearth to the crucible. The mechanism for this dross removal appears to be that the high energy electron beam breaks down the uranium and silicon oxides into higher vapor pressure sub-oxides which are then volatilized.

Total EB power input during the run was held constant at 230 kW and approximately 66% of this power was directed to the refining hearth and 34% to the crucible. The casting rate for this ingot was held fairly constant at ~370 kg/hr. as shown in Figure 4. Table 1 shows typical casting rates for VAR systems at the Y-12 plant which have roughly twice the capacity of the current LLNL 250 kW system.

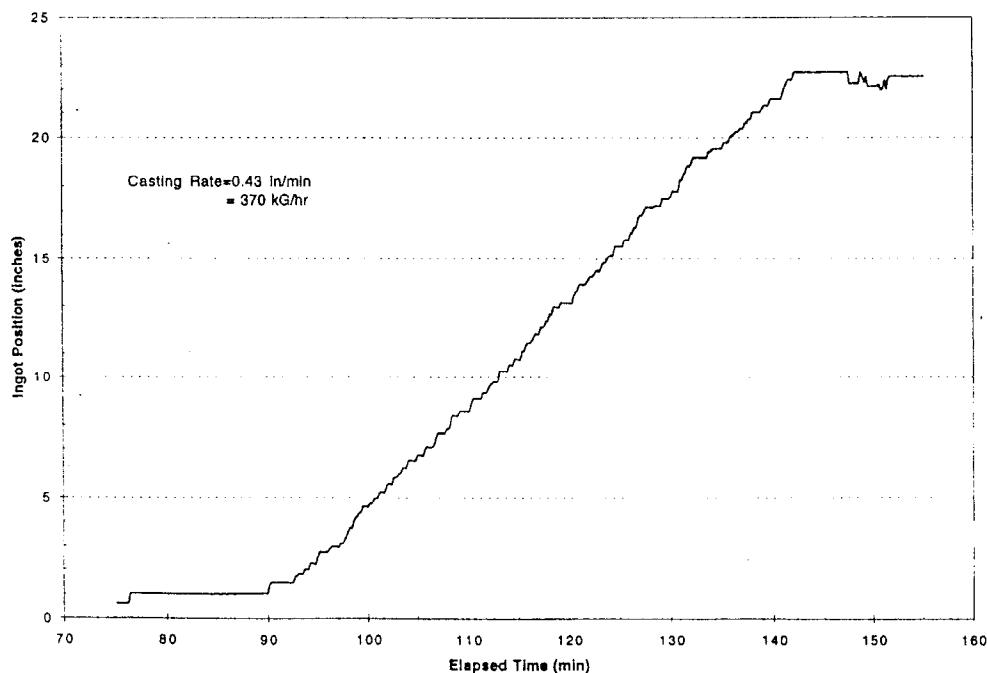


Figure 4: Ingot casting rate

| Process | Diameter - in. | Length - in. | Melt Rate - kg/hr |
|---------|----------------|--------------|-------------------|
| VAR | 8.25 | 30 - 40 | 630-900 |
| EB | 8.25 | 24 | 300-500 |

Table 1. Comparison of VAR and EB melting parameters

Characterization Procedures

The procedures used to characterize the EBCHR ingot closely followed the evaluations first devised by Y-12 [2,3] for standard VIM/SM/VAR product. A process flow diagram for these procedures is shown in Figure 5. The characterization efforts were organized into sectioning, wet chemical analysis, interstitial analysis, microprobe analysis and metallography. A somewhat detailed explanation of the procedures used for each of these operations is given below.

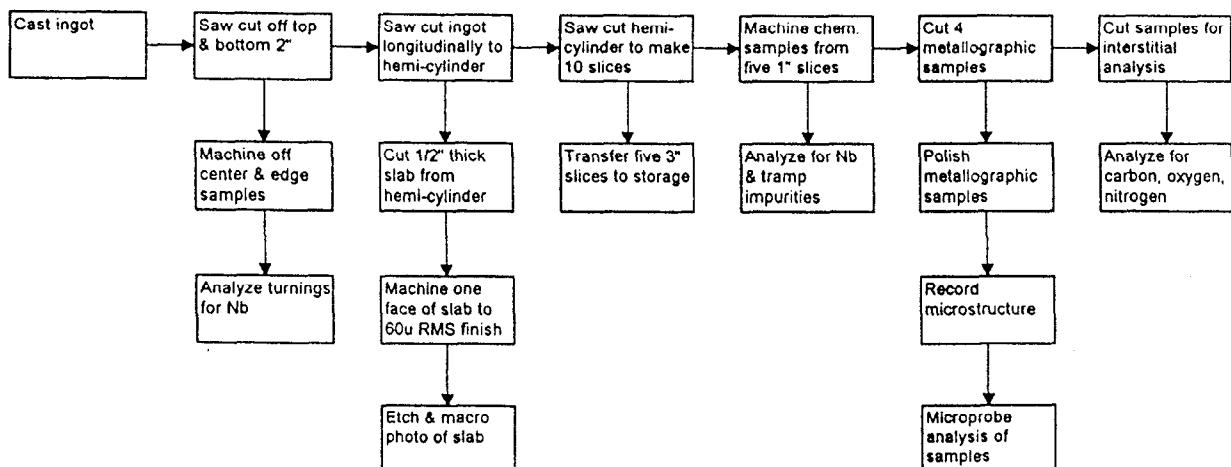


Figure 5: Ingot characterization flow sheet

1.0 Sectioning

All machining operations were performed using "Trimsol" water soluble lubricant. The following sectioning procedures were used:

1.1 Top and Bottom of Ingot for Chemical Analysis

The top 2" portion and the bottom 2" portion were cut from the ingot. Center and edge samples were obtained from the bottom of the top piece and the top of the bottom piece following standard Y-12 procedures [4] as shown in Figure 6.

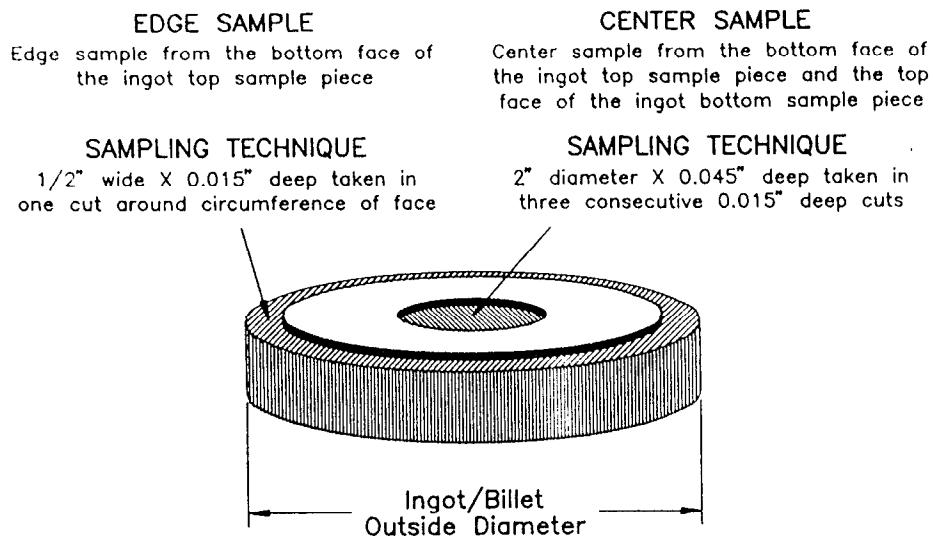


Figure 6: Standard Y-12 sampling procedure for Uranium - 6% Niobium alloy

1.2 Half-Ingot for XRF Macro Analysis

The remaining 20" long ingot was cut in half lengthwise to generate two hemi-cylinders. A ~1" thick slab (8.25" x ~20") was cut from the back hemi-cylinder, and the front (larger width) face of the slab was polished to a 16μ RMS or better finish. The polished slab surface was etched and photographed.

1.3 Ingot Slice Samples for Chemical Analysis

Slices from the front hemi-cylinder were cut at measured distances alternating from 1.1" and 3.0" along its length according to Figure 7. The top sides of the 1.125" thick slices were machined to a 120μ inch finish. 0.125" wide by 0.015" deep *radial* channels were then machined from the top faces of the samples as shown in Figure 8, at 0.5" intervals along the ingot radius.

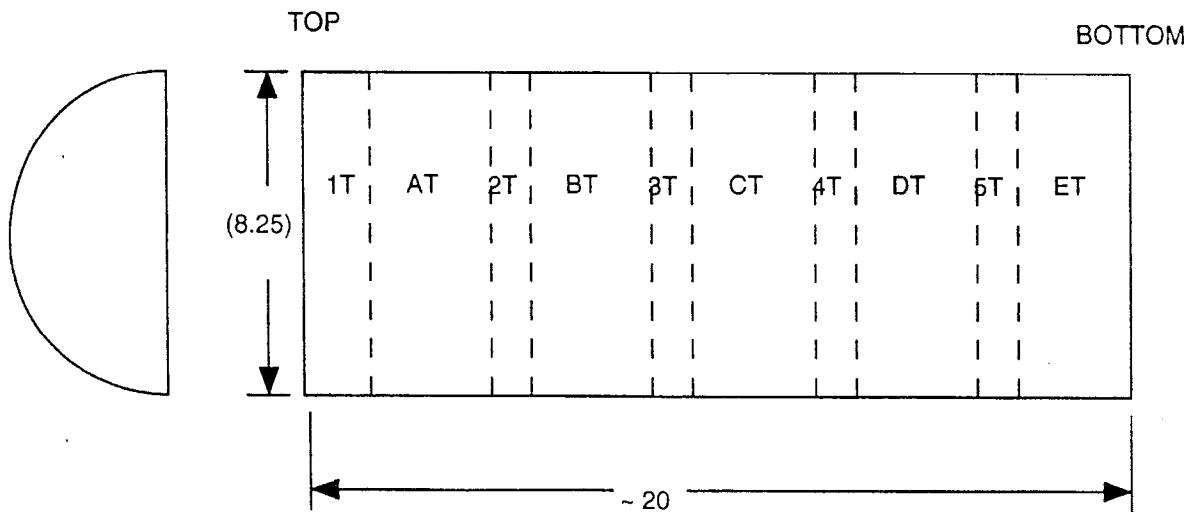


Figure 7: Hemi-ingot labeling and cutting

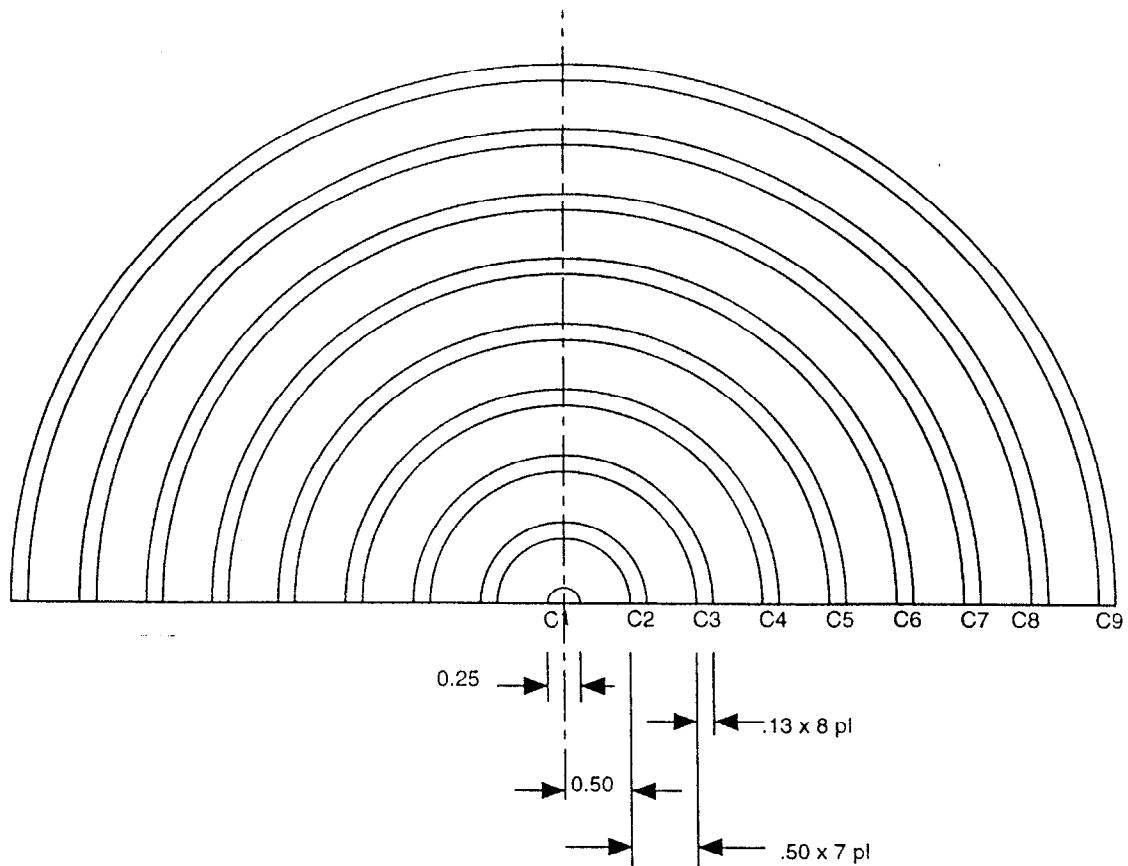


Figure 8: chemistry sample locations

1.4 Carbon/Oxygen and Metallographic Samples

Four cubes approximately 1" by 1" were cut from each 1" thick slice as shown in Figure 9.

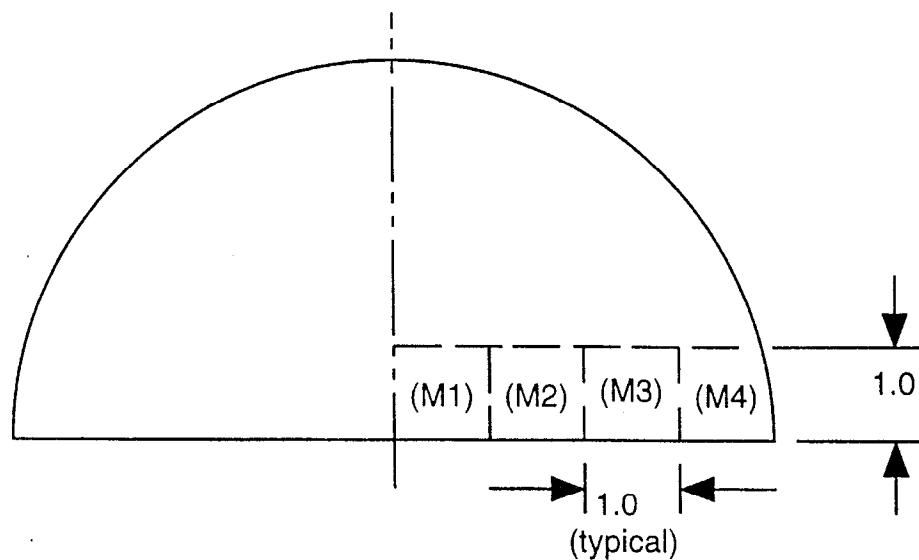


Figure 9: Ingot slice labeling

2.0 Chemical Analysis

Chemical analysis of the ingot was performed using the following procedures:

2.1 Niobium and Trace Metallics

Machine turnings from the top and bottom pieces, and from ingot slices obtained in section 1.3 were analyzed for niobium and trace metallics via Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) using standard Y-12 analytical procedures [5]. Three samples, approximately 1 gm each, were taken for analysis at each location. All samples were ultrasonically cleaned in detergent and rinsed in H₂O followed by ethyl alcohol. Chip samples were dissolved in acid and analyzed for uranium, niobium and trace metallics.

2.2 Carbon, Oxygen and Nitrogen

Samples generated in section 1.4 were analyzed for C, O, and N using standard LECO combustion equipment. Approximately 2mm cubes were cut from the bottom face of each metallography cube using a diamond saw wheel, and electropolished in a solution of 90% acetic, 10% perchloric acid. Samples were etched in 1N HNO₃ for 1 minute to remove all oxides then rinsed in de-ionized water, dried and immediately stored in acetone until ready for analysis. Typically, analysis was performed within 1 hour of cleaning. Samples were then analyzed for Carbon, Oxygen an Nitrogen.

3.0 Metallography and Microprobe

The 1" cubes generated in section 1.4 were examined for grain size, niobium dendritic microstructure, and carbide and oxide size and distribution using the following procedure:

The top face of each 1-inch cubes of U-6Nb was polished using established procedures for uranium alloys. Samples were oxidized in room temperature air to bring out structures of interest. Carbide and oxide inclusions, grain size and microstructure were then observed and recorded in digital format.

Selected 1" cubes were examined via electron microprobe techniques for niobium variations on a micro scale.

Results

Full ingot slice

A photograph of the ingot slice showing typical U-Nb banding is shown in Figure 10. Banding is a result of solidification dynamics for this particular alloy system and indicate areas of high and low niobium within the ingot on a macro scale. The liquid pool at steady state, as judged from the band profiles is about 1.3" deep compared with a pool depth of around 4"[6] for typical VAR product. EB processing gives the ability to independently vary rate and power input to promote shallow or deep pools as desired for a particular metal. In the case of the U-6Nb alloy, a shallow pool is desired to minimise banding. To promote this desired shallow solidification front, power was input to the ingot as a ring shaped beam directed to the periphery of the ingot only. As a result, banding appears less pronounced in the center of the ingot compared to the edge regions. It should be remembered, however, that this ingot was cast at roughly 2/3 of the nominal VAR rate so that a somewhat shallower pool would be expected. Note also the absence of porosity throughout the ingot. Electron beam hot topping was used to insure a completely sound ingot.

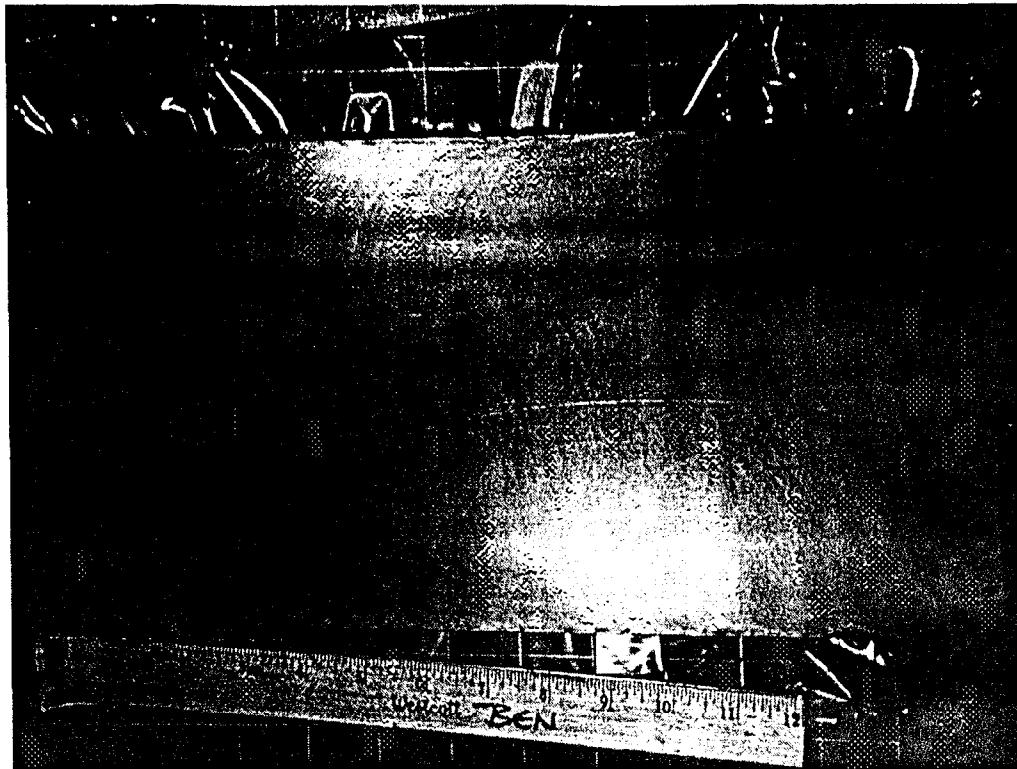


Figure 10: U-6Nb ingot slice showing banding

Ingot top and bottom

Analytical results for the feed material, and the ingot top and bottom (center and edge) for niobium and trace metallic elements are shown below in Table 2. Niobium is within the specified range of 5.2-6.5 percent by weight in the three areas of merit for the Y-12 specification: Top center and edge, and bottom center. As with VAR melted ingots, niobium analysis of the edge sample 2" up from the bottom of the ingot is high. It should also be noted that only 2" of material was removed from top of the EB melted ingot prior to analysis as compared with 4.6" in standard Y-12 melted material[7].

Previous Y-12 investigations [8] on purification of uranium by electron beam refining have shown substantial reductions in high vapor pressure metallic impurities after a single electron beam melt. Table 2 shows similar results for this current investigation. Chromium and manganese levels, the two high vapor pressure constituents measured, are preferentially lowered during electron beam processing. The more reactive metals (Mo, Ni, Ti and Zr) also appear to be somewhat lower in the ingot than in the feed although it is not clear if this is due to their higher vapor pressures with respect to uranium, or to their reactivity with carbon in the melt to form insoluble metal carbides. Overall, tramp impurities are lowered by EBCRH, resulting in a modest improvement in material purity. While it is known that certain tramp impurities affect corrosion resistance in the U-6Nb system, whether or not EB processing actually produces an improved product remains to be seen. The niobium appears to be slightly enriched compared to the feed, however as will be shown in the next section on niobium distribution within the ingot, this is at odds with results of niobium analysis for the individual ingot slices.

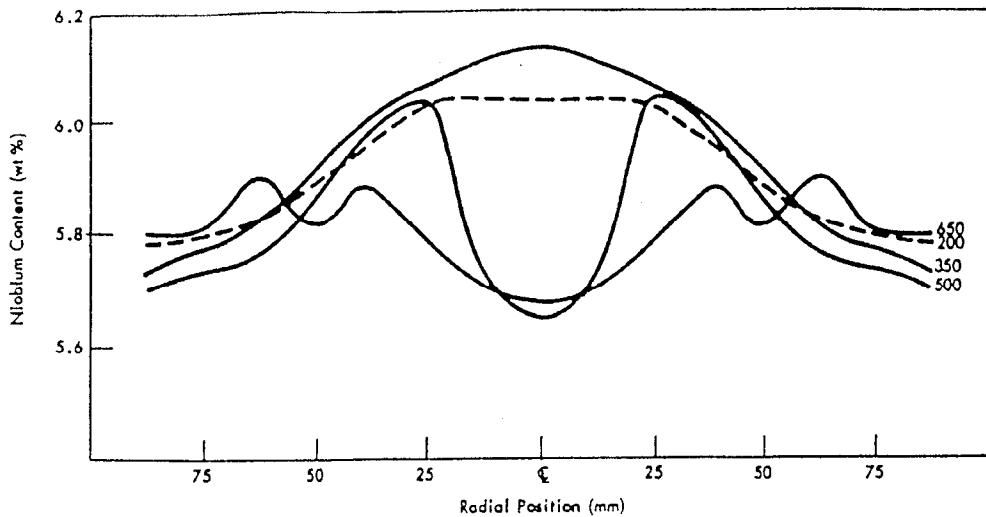
| | Nb | Al | Cr | Mn | Mo | Ni | Ti | Zr |
|----------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Spec. | 5.2-6.5* | 75 | | | 75 | 75 | 75 | 500 |
| Feed | 6.09 | 0 | 23 | 14 | 16 | 20 | 61 | 31 |
| Bottom-edge | 6.87 | 0 | 7 | 2 | 2 | 18 | 73 | 18 |
| Bottom-center | 6.28 | 0 | 7 | 4 | 6 | 14 | 61 | 16 |
| Top-edge | 6.31 | 0 | 15 | 8 | 18 | 15 | 56 | 22 |
| Top-center | 6.18 | 0 | 26 | 4 | 8 | 20 | 66 | 22 |

* The Y-12 specification [4] calls for niobium analysis of the top center and edge and the bottom center only.

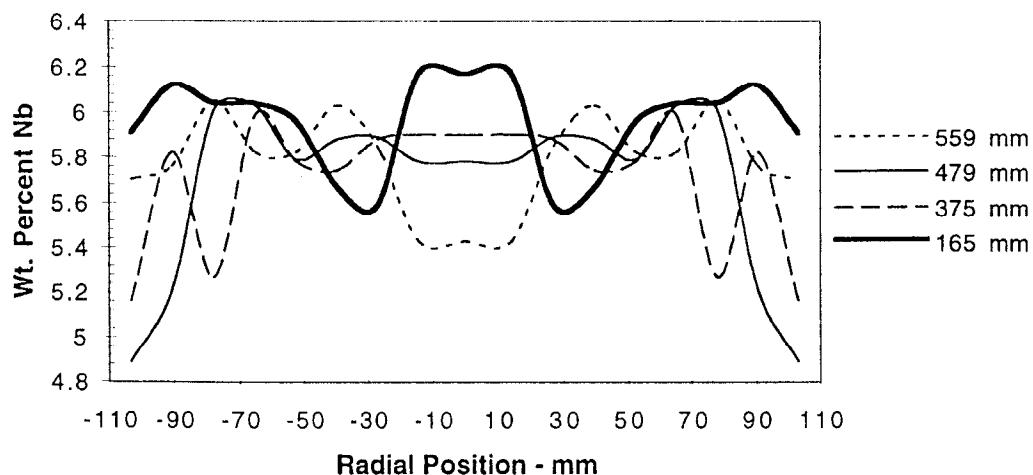
Table 2. Ingot top and bottom analysis

Niobium distribution

Niobium distribution as a function of both radial position and top to bottom location within the ingot are shown in Figure 11 for both the typical VIM/ SM/ VAR material and the EBCHR material. From these curves, it can be seen that in both cases, niobium tends to be higher in the center of the ingot near the bottom of the ingot whereas toward the top of the ingot, the situation reverses and niobium is lower in the center. Various theories have been put forth in the literature for the solidification patterns seen in this alloy, some of which imply that judicious programming of the electron beam on the ingot during casting may lead to more optimal ingot structures. For this particular set of casting conditions, however, EBCHR appears to produce a product comparable to the standard Y-12 material.



a) Typical VIM/SM/VAR material



b) EBCHR melted ingot

Figure 11: Edge to center niobium distribution in 210 mm diameter ingots at given distances above bottom of ingot

Carbon, Oxygen and Nitrogen

Plots of carbon, oxygen and nitrogen as a function of radial position and longitudinal location within the ingot are shown in Figure 12. From this data, it appears that carbon may be reduced slightly during melting whereas oxygen and nitrogen show slight increases. These small changes, however, are probably not statistically significant, especially since free energy calculations for oxygen and uranium oxide reacting in the liquid state show that this is not a favored reaction. This is also consistent with Y-12 experience on oxygen and nitrogen levels in VAR ingots [9].

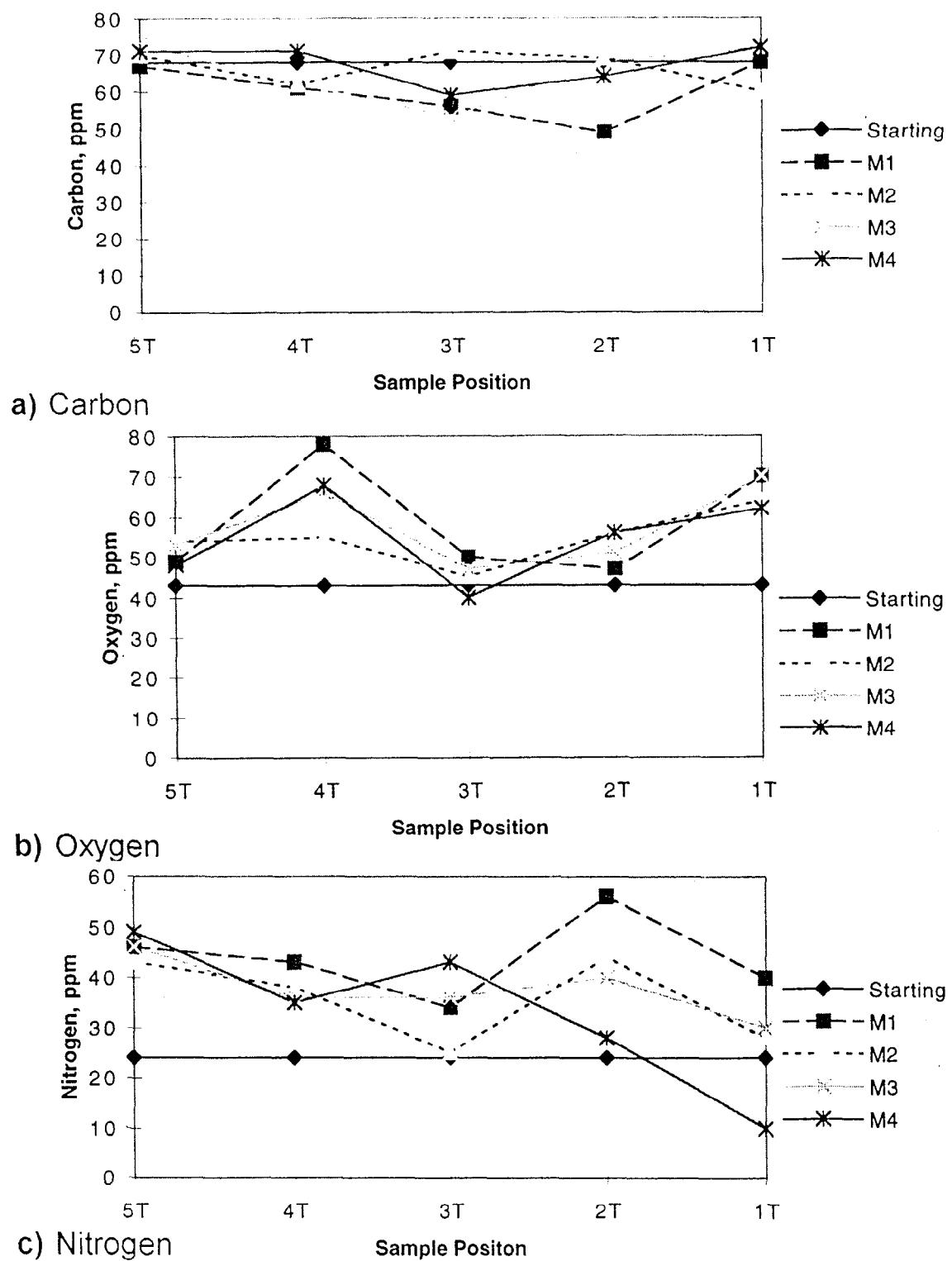


Figure 12: Interstitial element levels in EBCHR ingot

Metallography

Metallographically, the material appears similar to the baseline Y-12 U-6Nb. Grain size, center to edge, and distribution and size of inclusions appear typical of the VIM/ SM/ VAR material. The material appears free of major inclusions and voids. Figure 13 is a typical metallographic photo showing that carbides are randomly distributed and all below 20 microns in size.

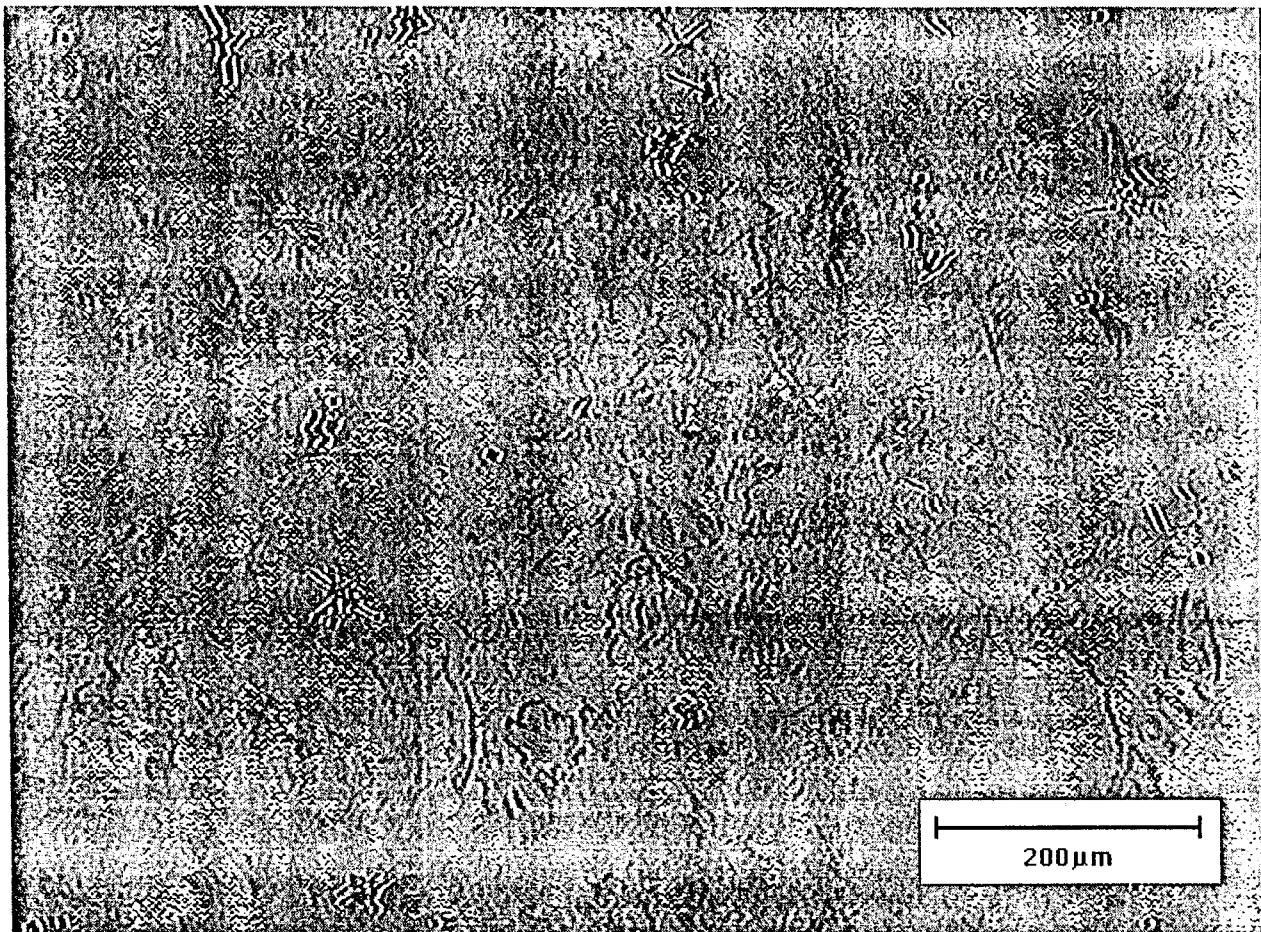


Figure 13: Metallographic photo

Microprobe analysis

A plot of electron microprobe scans of both the VIM/ SM/ VAR and the EBCHR material is shown in Figure 14. As expected, since the interdendritic coring giving rise to these micro-variations are a function of the particular alloy system rather than processing conditions, the EBCHR material looks very similar to the standard VIM/SM/VAR material [10].

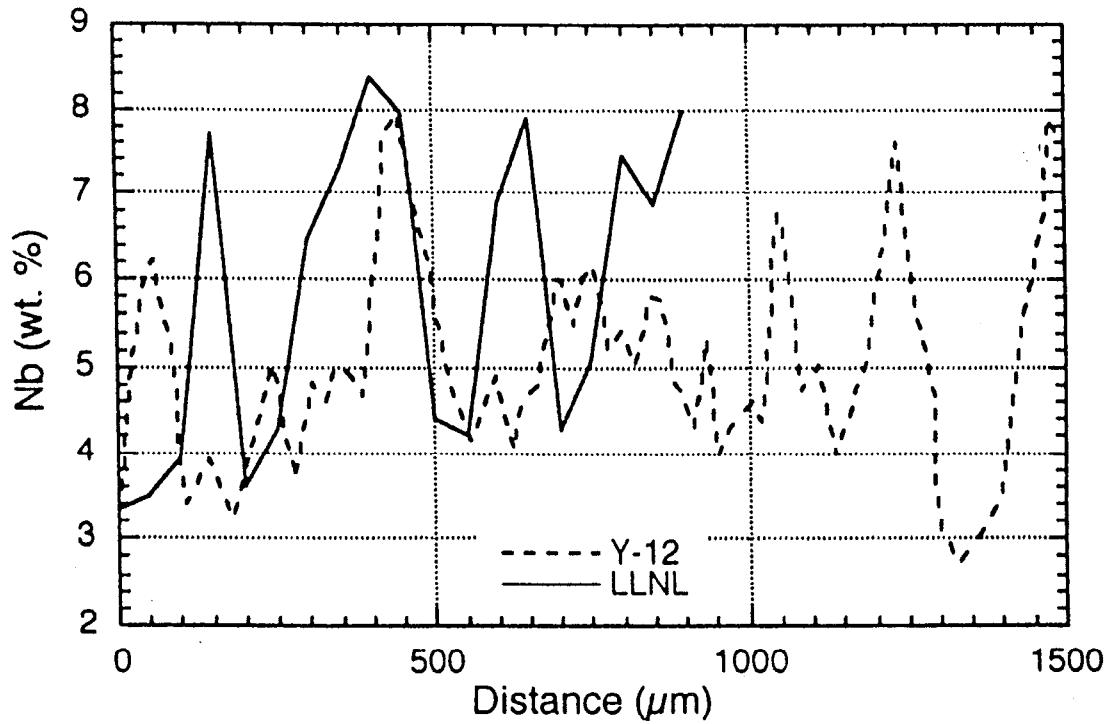


Figure 14: Macrosegregation in U-6Nb ingots

Discussion

This EBCHR ingot produced from 100% recycled scrap plate appears to be comparable to the standard Y-12 product in all areas studied. Gross segregation (top-bottom) is comparable. Macro-segregation (banding) of the EBCHR material appears to be slightly less distinct than in the standard Y-12 material. Micro-segregation (dendritic coring) is same as for the Y-12 material. Carbon, oxygen and nitrogen appear to be unchanged by EB processing, whereas in the Y-12 material, carbon is increased by about 50 ppm with each melt. The slight differences seen between Y-12 reported results and LLNL reported results probably have more to do with differences in analytical equipment and techniques between the two institutions than in actual variations in ingot chemistries.

One of the limitations in electron beam processing is maintaining correct chemistry when melting alloys. Higher vapor pressure metallic constituents tend to be preferentially evaporated and are depleted in the final ingot. Both uranium and niobium, however, have very low vapor pressures at processing temperatures and evaporative losses during electron beam melting of U-6Nb are quite low - typically less than 0.5% in the LLNL furnace. Gross ingot chemistry, therefore, is strictly dependant upon the chemistry of the feed stream. Moreover, the only losses in the process are croppings from the ingot top and bottom, which, because EBCHR is a non-contaminating process, can be recycled indefinitely.

This study has shown that a single EBCHR melt can produce uranium 6% niobium ingot material meeting current specifications and which appears comparable to the baseline, triple melted material. The technology development phase of this project is considered to be complete, and the process is now ready to be transferred to the Y-12 production facility where further characterization and statistical comparisons will need to be made prior to final certification of the process. With the current reduced level of parts needed, and an approximate capital investment of \$2.5 M needed to install an EBCHR facility at Y-12 however, there is no plan to replace Y-12 baseline in the foreseeable future. Components are at present being fabricated from EBCHR ingot material, and will be evaluated over the course of the coming year.

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