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ELECTROSLAG REMELTING OF A URANIUM ALLOY

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ABSTRACT

A method for electroslag remelting (ESR) of a uranium alloy was developed which reduced the oxygen content from 200-300 ppm to less than 50 ppm. Slag compositions included acid grade CaF_2, reagent grade CaF_2, $CaF_2 \cdot Ca$ and $CaF_2 \cdot MgF_2$ in ESR melting a uranium-7.5 wt % niobium-2.5 wt % zirconium alloy.

Equipment and techniques were developed for dry slag starts and dry slag additions during melting. The effects of straight polarity versus reverse polarity were examined as well as the effectiveness of stirring.

Microexamination of the slag after melting was made and the chemical composition was determined. The uranium alloy was also examined chemically and microscopically for the size and distribution of inclusions. A comparison of alloy segregation was made between vacuum arc remelted material and the electroslag remelted material by radiography.

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ELECTROSLAG REFINING OF A URANIUM ALLOY

J. L. Cadden and P. S. Lewis, Jr.

INTRODUCTION

During the last two decades, the Y-12 Plant at Oak Ridge, Tennessee, has produced numerous uranium alloys by methods such as: co-reduction from uranium hexafluoride, vacuum induction melting, consumable and non-consumable vacuum arc melting, vacuum skull casting, and more recently, by the ESR or electroslag refining.

Our interest in ESR melting arose from a need to find a suitable method of reducing the oxygen content of machine turnings of a uranium-7.5 wt % niobium-2.5 wt % zirconium alloy. The alloy, referred to as Mulberry, was being produced by the consumable vacuum arc melting process. Electrodes were made by sandwiching strips of uranium, niobium, and zirconium together and melting into a 127 mm (5-inch)-diameter crucible followed by a second melt into a 178 mm (7-inch)-diameter crucible.

A successful recycle method had been developed for the alloy using only cleaned massive scrap which was diluted 50% with virgin material in a skull caster. Attempts to blend in machine turnings had failed due to a sharp rise in oxygen content. Oxygen at this level produced unsatisfactory material because of the formation of large oxide agglomerates which caused poor mechanical properties and surface flaws. A comparison of the average analysis for the various types of Mulberry is noted in Table 1.

The VAR process also produced an ingot which contained banding segregation and an inverse segregation of the niobium from the outer periphery of the ingot to the core.

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Table 1

COMPARISON OF AVERAGE ANALYSES FOR MULBERRY ALLOY

	Production Processes			
Element	Virgin	Massive Recycle	Blended Recycle	Chip Melts
U (%)	89.98	89.89	89.93	89.74
Nb (%)	7.53	7.61	7.54	7.70
Zr (%)	2.47	2.47	2.45	2.42
C (ppm)	62	63	62	72
Fe (ppm)	52	56	103	209
Cu (ppm)	11	13	19	11
O_2 (ppm)	65	73	132	200-1600
Si (ppm)	50	70	100	150

The banding segregation is illustrated in Figure 1 which is a positive reproduction of a radiograph obtained from a 3.2 mm (1/8-inch)-thick longitudinal section from the center of the ingot. Numerous attempts at reducing the banding by altering the VAR conditions, i.e., voltage, amperage, feed rate, and stirring, had little effect.

The inverse segregation is illustrated in Figure 2 which is a plot of the niobium content at various radii across the face of a 178 mm (7-inch)-diameter ingot.

The above reflects an inverse segregation mechanism occurring during solidification. The terminology "inverse segregation" is used with this alloy system since the niobium increases the liquidus temperature. Normal segregation would give lower niobium at the ingot center and top.

We surmised that as the ingot solidifies, it shrinks away from the wall of the crucible resulting in poor heat transfer. This shrinkage, in turn, reduces the thermal gradient and produces a thick, mushy zone.

The shape of the solidification front is illustrated in Figure 3. As dendritic growth occurs, niobium-rich crystals are first to freeze depleting the adjacent liquid in niobium. Solidification shrinkage causes an inward flow of niobium-depleted liquid and thus inverse segregation. The occurrence of interdendritic porosity at the centerline indicates inadequate flow of liquid feeding the shrinkage.

A change in heat input resulting from arc wander or arc shorting can disturb the solidification process. This change in rate of solidification was thought to produce the banding observed by radiography.

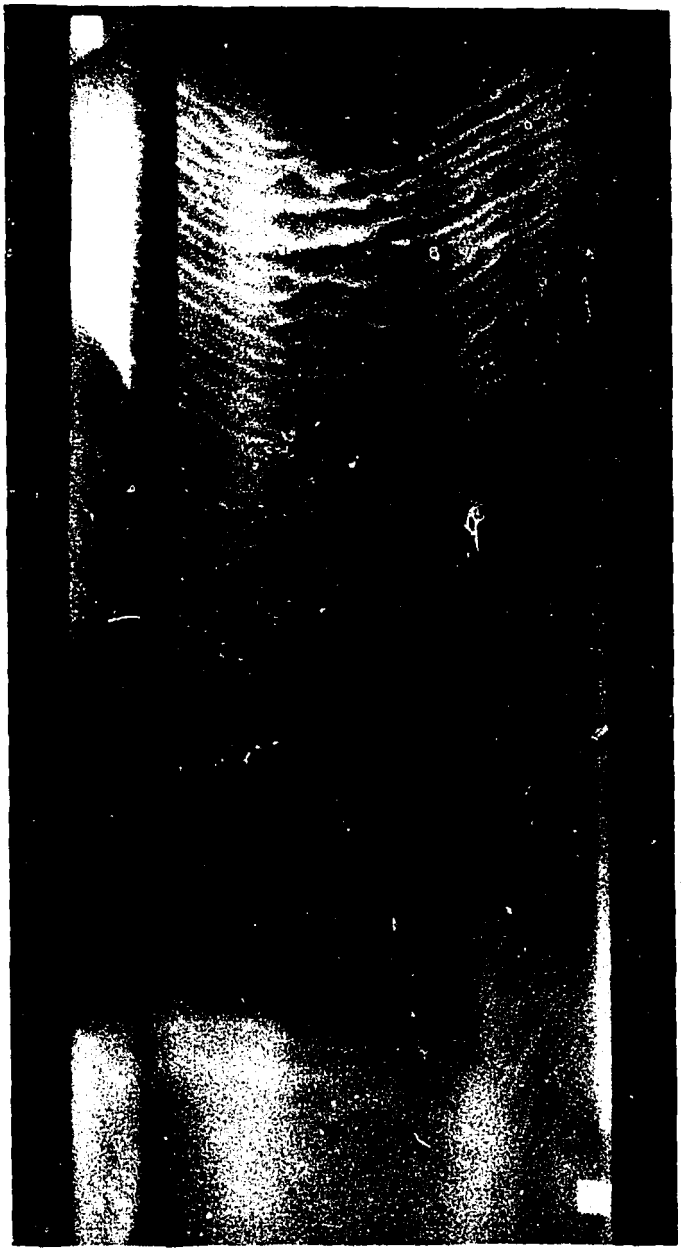


Figure 1. RADIOGRAPH OF A 0.125-INCH-THICK, VERTICAL SLICE FROM A VAR-MELTED URANIUM-7.5 WEIGHT PERCENT NIOBIUM-2.5 WEIGHT PERCENT ZIRCONIUM ALLOY INGOT.

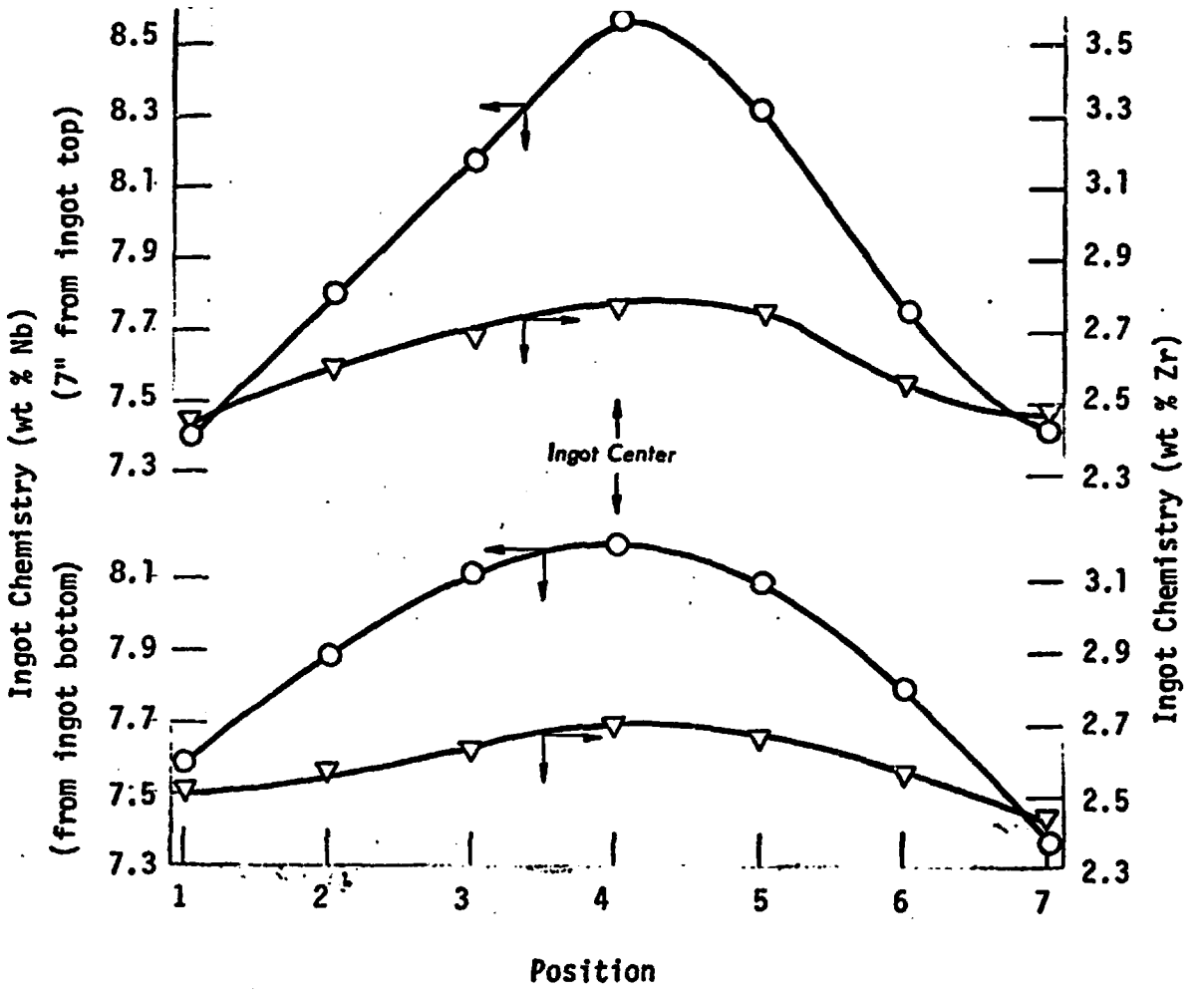


Figure 2. NIOBIUM AND ZIRCONIUM ANALYSES FROM THE INGOT MELTED AT A CONSTANT CURRENT OF 6,000 AMPERES. (Note that Niobium Varies much more from Edge to Center at the Top than at the Bottom)

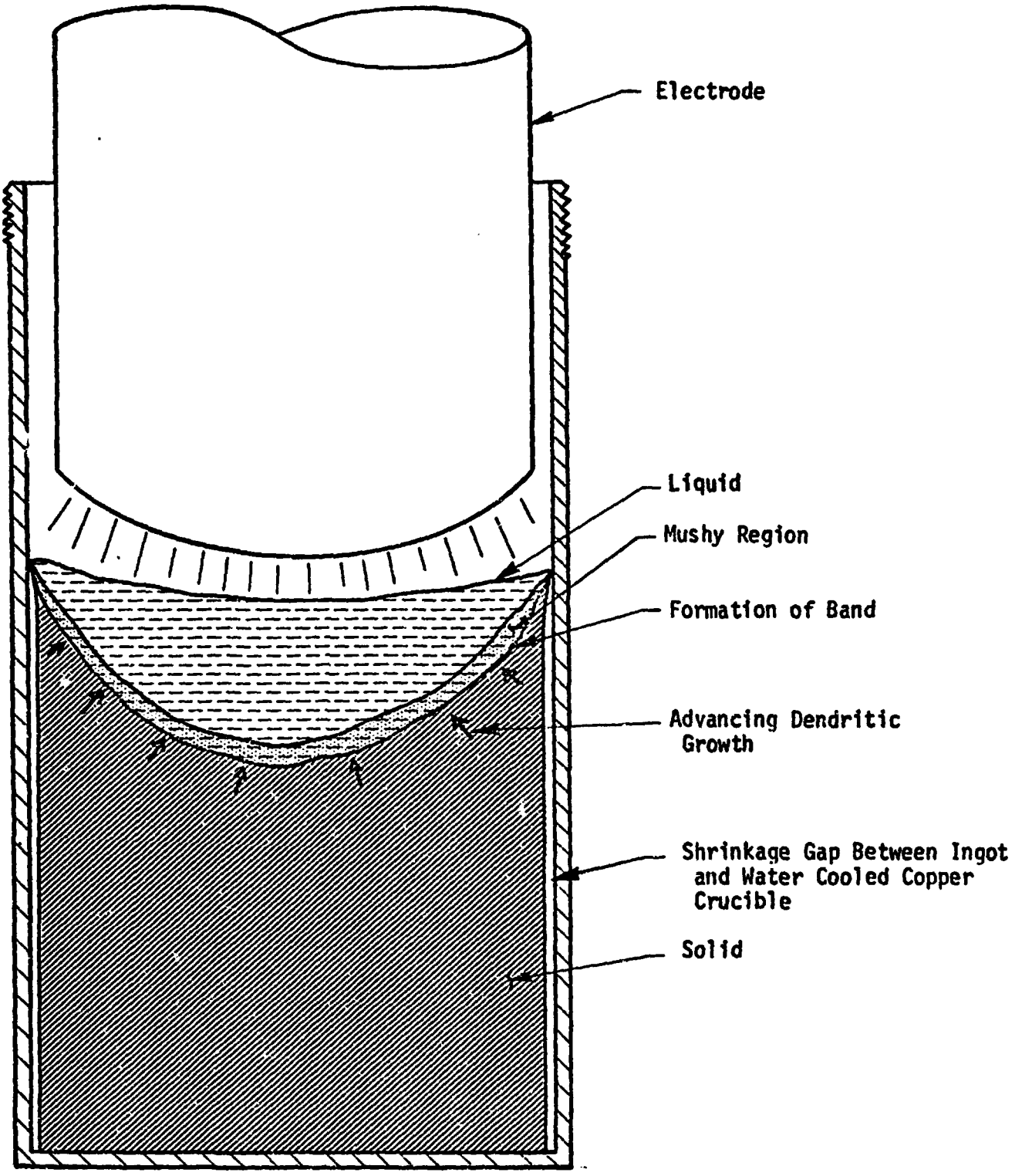


Figure 3. SEGREGATION OCCURRING DURING VAR MELTING OF A U-Nb-Zr ALLOY

It was surmised that the slag during ESR melting would fill in around the ingot as it shrinks away from the crucible wall and thereby promote improved heat transfer, hence less inverse segregation of the niobium. Also, it was hoped that resistance melting through the slag would "insulate" the melt from sudden changes in heat input as observed with an arc and thereby reduce the banding segregation.

Other benefits of the ESR technique which appeared attractive included the possibility of a smaller pipe cavity at the top of the ingot and an improved ingot surface which would not require machining for subsequent operations. ESR melting was also considered as being safer since the elimination of the arc would reduce the potential for cup damage.

EQUIPMENT

The techniques for ESR melting of the Mulberry alloy were developed on a Consarc 8-inch Laboratory Furnace which is ideally suited for this type of work. The furnace, as shown in Figure 4, is designed for making both ESR and VAR melts in a closed system under vacuum or a partial pressure of an inert gas. The power supply consists of ten D.C. units arranged to furnish 10,000 amps at 40 volts. These rectifiers are controlled as a unit during a melt, but changes in voltage or current must be made manually. The electrode drive may be controlled manually, or by arc voltage using a preset reference voltage, or by detection of ionized columns of metal vapors (called "Phantom" short circuits). The vacuum system consists of a mechanical pump for roughing and holding and two 4-inch oil diffusion pumps. Two melt stations, designed for live mold operation, are available. One station is equipped with electromagnetic stirring coils having a 0 to 25 gauss capability for single, cyclic, or double mode stirring.

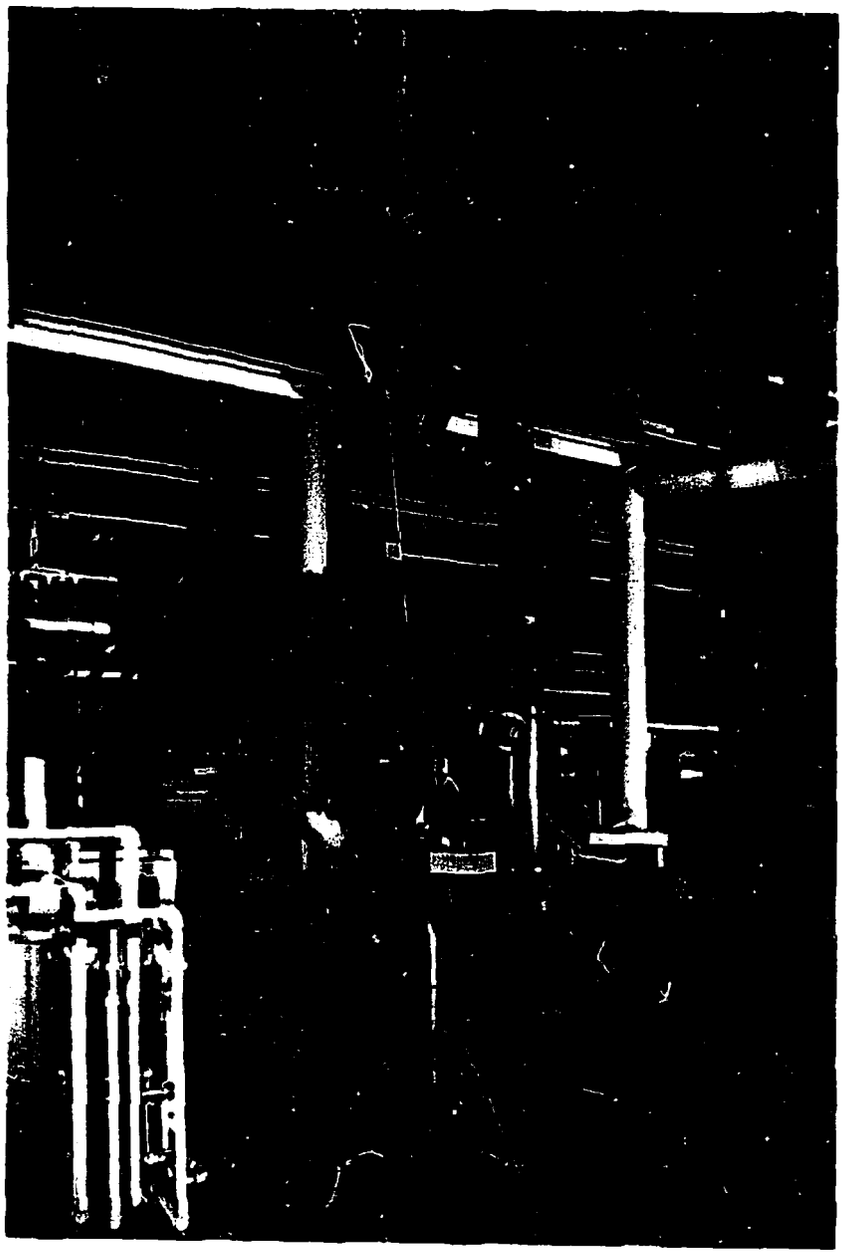


Figure 4. EIGHT-INCH-DIAMETER CONSARC LABORATORY FURNACE

A second 20-inch-diameter Consarc Furnace was also available to make selected 10-inch-diameter melts. Both furnaces are designed for dry slag starts. A separate chamber contains a hopper to hold the slag materials, a vibrator chute to control the feed rate and deliver the dry slag to the crucible, and a ball valve to isolate the chamber from the furnace proper. A second vibrator has been attached to the storage hopper to eliminate bridging.

EXPERIMENTAL WORK

Our first task for this investigation was to find a suitable slag. Since uranium is a very active metal, the list of materials for ESR slags is short. Most of the common components of commercial slags are eliminated because of the reactivity of uranium with oxide-containing materials. This coupled with vapor pressure restrictions at operating temperatures and pressures generally limited our choice of constituents to the following fluorides: LiF, SrF_2, CaF_2, MgF_2, and R. E. (rare earth) fluorides.

It appeared that CaF_2 was the most suitable material since: 1. it is used almost universally as the principal constituent of ESR slags; 2. it is economically available; 3. it has a lower vapor pressure than other candidate materials; and 4. it is inert to molten uranium.

From the Molten Salt Reactor Program, investigators at the Holifield Oak Ridge National Laboratory had observed that oxides are more soluble in an acidic or basic slag than in a neutral slag such as CaF_2. It was also known that an ESR slag should have a melting point at least 200°C lower than that of the metal to be melted. Since CaF_2 has a melting point of 1410°C compared to 1310°C for Mulberry, additions of MgF_2 would

not only drop the slag M.P. but also increase the acidity. Uranium alloy chips which had previously been degreased and chopped were briquetted into an electrode as shown in Figure 5.

Several unsuccessful attempts were made at ESR melting these electrodes with CaF_2 slags containing 5-10 wt % MgF_2. The problem was surmised to be a result of the dissociation of the MgF_2 to Mg resulting in the arc shorting to the wall of the crucible and termination of the melt. From these melts, however, it was observed that the melting point of the slag did not appear to be as crucial as expected.

Consequently, our next melts were made with CaF_2 prefused with 0.5 wt % MgF_2. The slight addition of MgF_2 was made to promote solubility of the oxides in the slag. No difficulty was encountered in melting with the slag composition. The melting parameters are listed in Table 2.

Figure 6 is a photograph of a typical ingot from this series. As can be seen, some slag entrappment has occurred near the start of melting and is probably due to the addition of too much slag initially. The remainder of the surface is rough and has the appearance of gas entrappment at the slag-metal interface.

The chemical data from these ingots are listed in Table 3. As can be observed, the major constituents U, Nb, and Zr are within expected limits as is the C, Cu and N_2. The iron has increased indicating chip contamination. The silicon content has nearly doubled and the oxygen is erratic and considerably higher than desired.

Figure 5. BRIQUETTED CHIP ELECTRODE USED IN ESR MELTING STUDIES

Table 2

MELTING PARAMETERS FOR ESR MELTING BRIQUETTED CHIP ELECTRODES INTO 10-INCH-DIAMETER INGOTS

Slag Composition	Slag Weight Plan Fed In Hopper			Slag Cap Thickness		Melt Power		Furnace Pressure mm of Mercury	Ingot Weight
	kg	kg	kg	(mm)	(in)	volts	kiloamps		
CaF_2 - 0.5 wt % MgF_2	20	20	0	127	5	17-22	6.0-8.0	25.4	280
CaF_2 - 0.5 wt % MgF_2	20	20	0	140	5½	17-23	5.5-9.0	25.4	296
CaF_2 - 0.5 wt % MgF_2	20	20	0	127	5	18-20	5.5-9.0	25.4	291
CaF_2 - 0.5 wt % MgF_2	20	20	0	115	4½	18-19	5.5-8.5	25.4	315

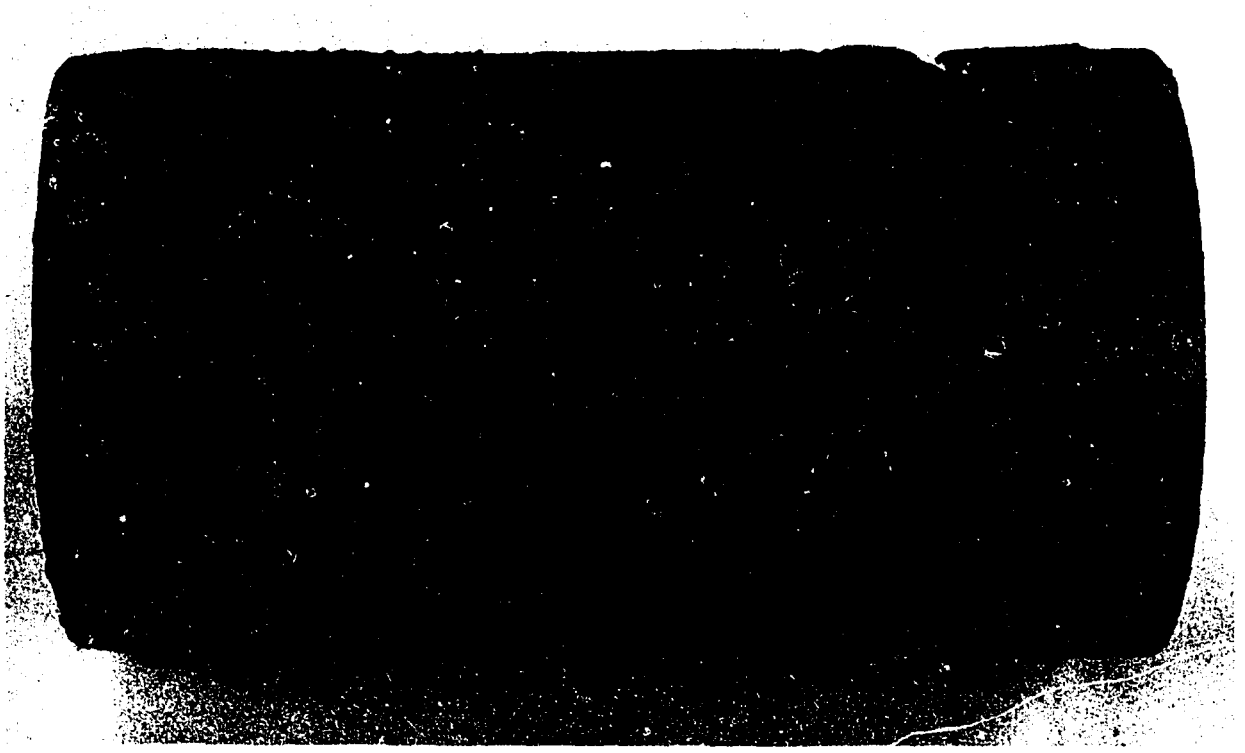


Figure 6. TYPICAL 254 mm INGOT RESULTING FROM ESR MELTING A BRIQUETTED CHIP ELECTRODE WITH A CaF_2-0.5 wt % MgF_2 SLAG

Table 3

CHEMICAL DATA OBTAINED FROM INGOTS ESR MELTED
USING CaF_2-0.5 wt % MgF_2 SLAG AND A BRIQUETTED CHIP ELECTRODE

URANIUM %		NIOBIUM %		ZIRCONIUM %		CARBON ppm		COPPER ppm		IRON ppm		SILICON ppm		NITROGEN ppm		OXYGEN ppm					
																T			B		
T*	B**	T	B	T	B	T	B	T	B	T	B	T	B	T	B	1	2	3	1	2	3
89.7	90.4	7.9	7.3	2.5	2.4	54	152	2	2	200	200	150	200	14	20	107	145	1131			
89.6	89.9	8.1	7.4	2.5	2.4	84	138	4	4	200	200	200	350	18	20	399	105	151	112	100	11[illegible]
89.1	90.2	8.0	7.4	2.4	2.4	58	81	4	40	200	250	175	250	89	12	181	88	459	134	99	21[illegible]
89.6	90.3	8.2	7.7	2.5	2.4	64	50	4	25	175	175	125	175	25	18	215	111	131	63	78	9[illegible]

* Top

** Bottom

One of the ingots was subsequently processed into plate and sectioned for metallographic examination. Figure 7 reveals the microstructure of ESR melted alloy. The ESR material contains numerous small oxide inclusions. The size and uniform dispersion of the inclusions prompted an examination of the slag caps from these ingots.

The slag caps contained two distinct regions: a 3 to 3-1/2" gray layer on top and a red layer next to the ingot. The slag samples were examined by optical and scanning electron microscopes. Particulate material, which showed a ruby red color under polarized light which is typical of uranium oxide, was observed in the red layer next to the metal. These particles appeared to have metal centers and nonmetallic deposits outside. Only uranium, zirconium, and oxygen were found when these particles were analyzed by electron microprobe. The morphology of the particulates was strongly suggestive of formation by precipitation from solution. To check this thesis, the slag material was remelted under argon and both slow cooled and rapid quenched. The quick quenched specimen showed a uniform distribution of particulates, whereas the slow-cooled specimen showed a band of particulates around a center shrink cavity. These data suggest that the oxide particles in the electrode are dissolved in the slag, reprecipitated in the metal pool, and with rapid solidification, appear in the microstructure as finely dispersed particles.

One method for producing uranium metal is by the bomb reduction of oxides using calcium metal as the reducing agent. This prompted our next series of melts in which Ca metal was added as granules to the CaF_2-0.5 wt % MgF_2 slag. Melting conditions were similar to the previous CaF_2-0.5 wt % MgF_2 slag melts.

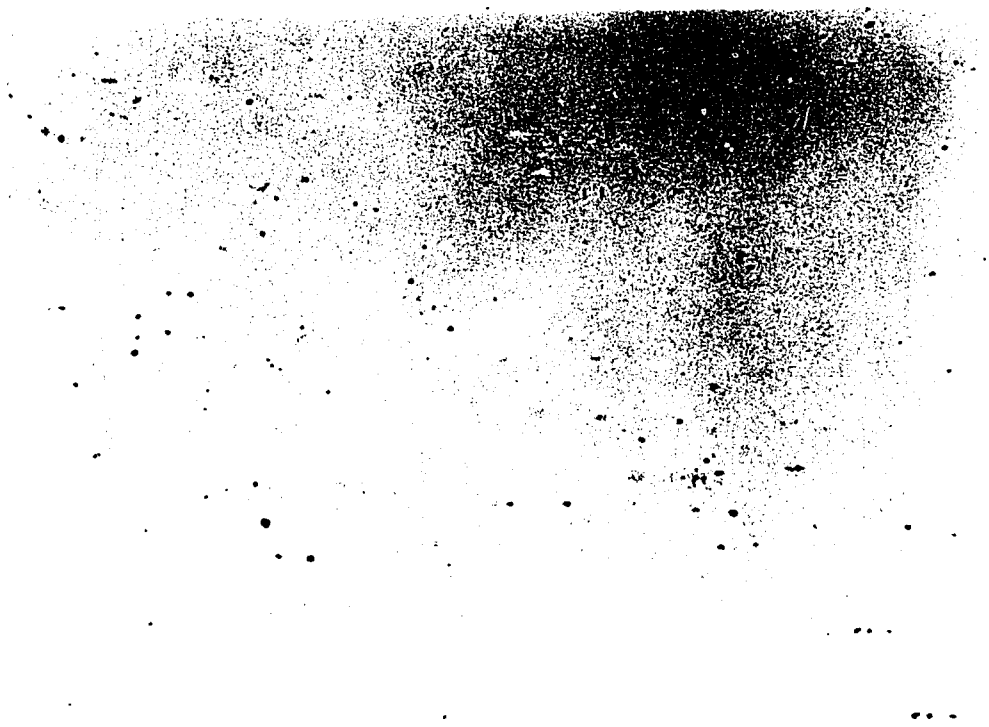


Figure 7. PHOTOMICROGRAPH SHOWING SMALL, EVENLY DISPERSED OXIDE INCLUSIONS IN ESR PROCESSED URANIUM-7.5 WEIGHT PERCENT NIOBIUM-2.5 WEIGHT PERCENT ZIRCONIUM ALLOY USING CALCIUM FLUORIDE SLAG. (As Polished, Bright Field Illumination - 100X)

The oxygen and silicon results from this campaign are contained in Table 4. The oxygen contents do not show an improvement and there appears to be a segregation of the oxide to the top center of the ingot. The silicon content has also remained about the same as the ingots melted with the CaF_2-0,5 wt % MgF_2 slag.

There was, however, a significant improvement with respect to slag fluxing and ingot surface with the Ca addition as shown in the photograph of the ingot in Figure 8. There was only a trace of unmelted slag in the bottom and the surfaces were much brighter in appearance.

In searching for the cause of the silicon contamination, analysis of the CaF_2 was made. The acid grade CaF_2 was used and contained 0.7 wt % SiO_2 and 0.8 wt % total oxygen. Reagent grade CaF_2 was obtained and analysis showed it to contain 0.02 wt % SiO_2 and 0.7 wt % total oxygen.

The silicon increase in the Mulberry made with the acid grade CaF_2 suggested that the SiO_2 in the slag was reduced by the uranium in the alloy.

To determine if silicon contamination could be prevented, reagent grade CaF_2 was purchased and used in the following three melts as CaF_2-0.5 wt % MgF_2-4.8 wt % Ca. The chip electrodes were also melted into 178 mm (7-inch)-diameter ingots rather than 254 mm (10-inch) diameter. The oxygen and chemistry results are listed in Table 5.

It is apparent from this data that the silicon contamination was indeed coming from the acid grade CaF_2 and that it could be eliminated by using the reagent grade. It is also apparent that a sufficient reduction in oxygen occurred over most of the length of the ingot but sufficient Ca was

Table 4

OXYGEN AND SILICON CONTENT OF INGOTS MADE BY ESR MELTING BRIQUETTE CHIPS IN A CaF_2-0.5 wt % MgF_2-4.8 wt % Ca SLAG

Oxygen ppm						Silicon ppm	
Top End			Bottom End				
1*	2	3	1	2	3	Top**	Bottom
100	96	88	101	98	95	400	300
410	89	114	80	81	74	200	400
2975	70	90	690	93	156	200	200
1548	76	90	73	85	81	100	200

* Samples obtained from (1) the ingot center, (2) mid-radius, (3) outer periphery.

** Samples obtained from entire face of the ingot.

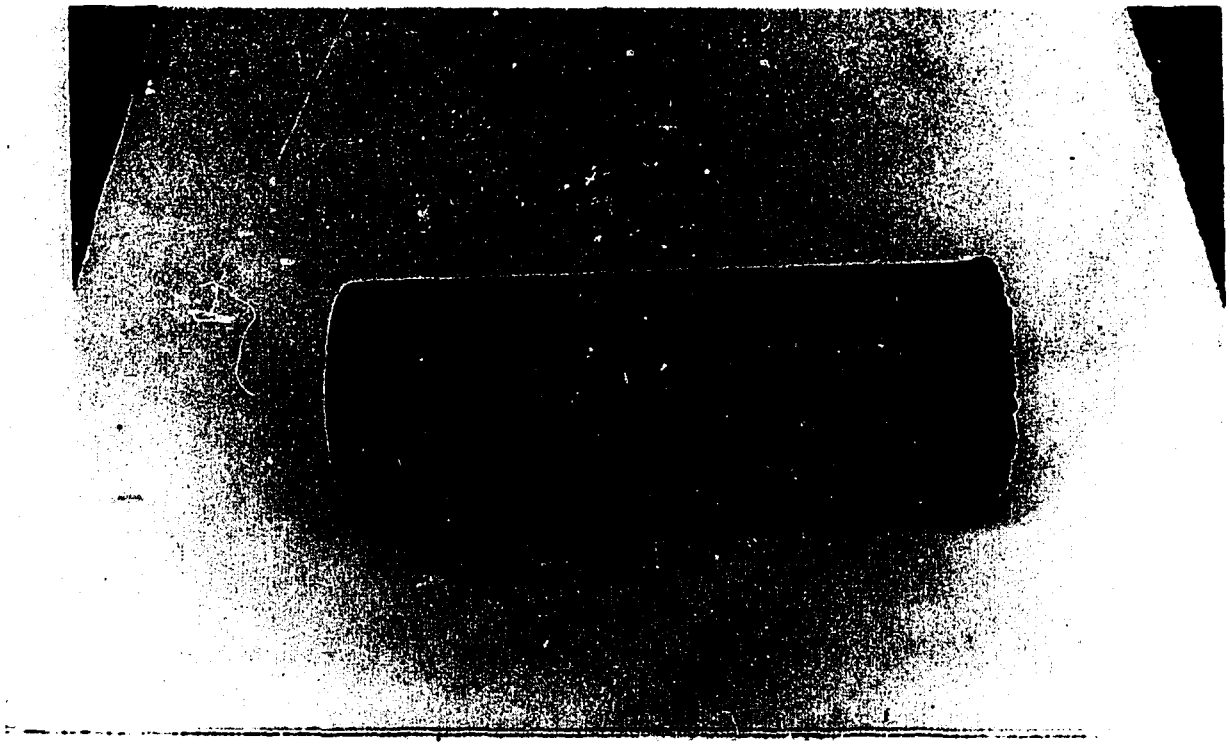


Figure 8. IMPROVED SURFACE OF ESR MELTED INGOT RESULTING FROM ADDITION OF Ca METAL TO THE SLAG

Table 5

OXYGEN AND SILICON CONTENT OF 178 mm (7-INCH)-DIAMETER INGOTS MELTED USING REAGENT GRADE CaF_2-0.5 wt % MgF_2-4.8 wt % Ca SLAG

Oxygen						Silicon	
Top			Bottom				
1	2	3	1	2	3	Top	Bottom
559	81	77	81	78	74	45	65
593	111	119	69	68	81	50	75
291	52	61	63	76	91	60	80

not available near the top causing a sharp rise in oxygen near the center.

Additional melts were made with the Ca content increased to 5.5 wt %. Also several melts were made without the MgF_2 addition to determine its importance. The oxygen results from the above melts are shown in Table 6.

It did not appear that the MgF_2 addition was increasing the solubility of oxygen in the slag since little difference was be observed between the slags which contained MgF_2 and those that did not. Oxygen reduction is a result of the Ca metal addition and by increasing the addition from 4.8 wt % to 5.5 wt % a sufficient supply was available at the top of the melt to eliminate the previously noted build-up.

The surfaces of these ingots were quite smooth and bright in appearance and did not require conditioning for subsequent processing. Figure 9 shows a typical ingot after removal of the slag skin.

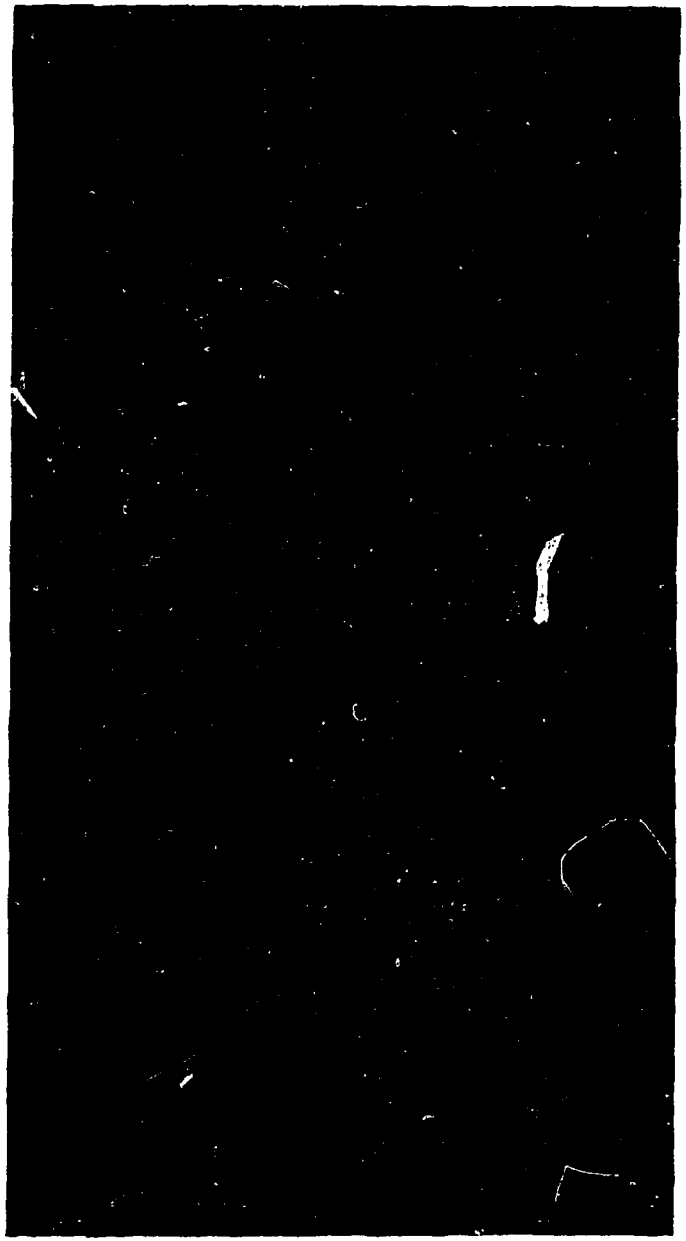
Figure 10 is a positive reproduction of a radiograph section taken of a 3.2 mm (1/8-inch)-thick longitudinal section from the center of the above ingot. Also shown in this figure for comparison is a radiograph of a similar sample taken from a VAR melted ingot. It does not appear that we have caused a great deal of change in the banding segregation by ESR melting. Apparently the banding is more closely associated with the freezing pattern of the ingot rather than fluctuations resulting from changes in heat input. The inverse segregation has been improved as can be seen in Figure 11. Although the improvement is slight with respect to chemistry, a more dramatic improvement is associated with the uniformity of mechanical properties.

Table 6

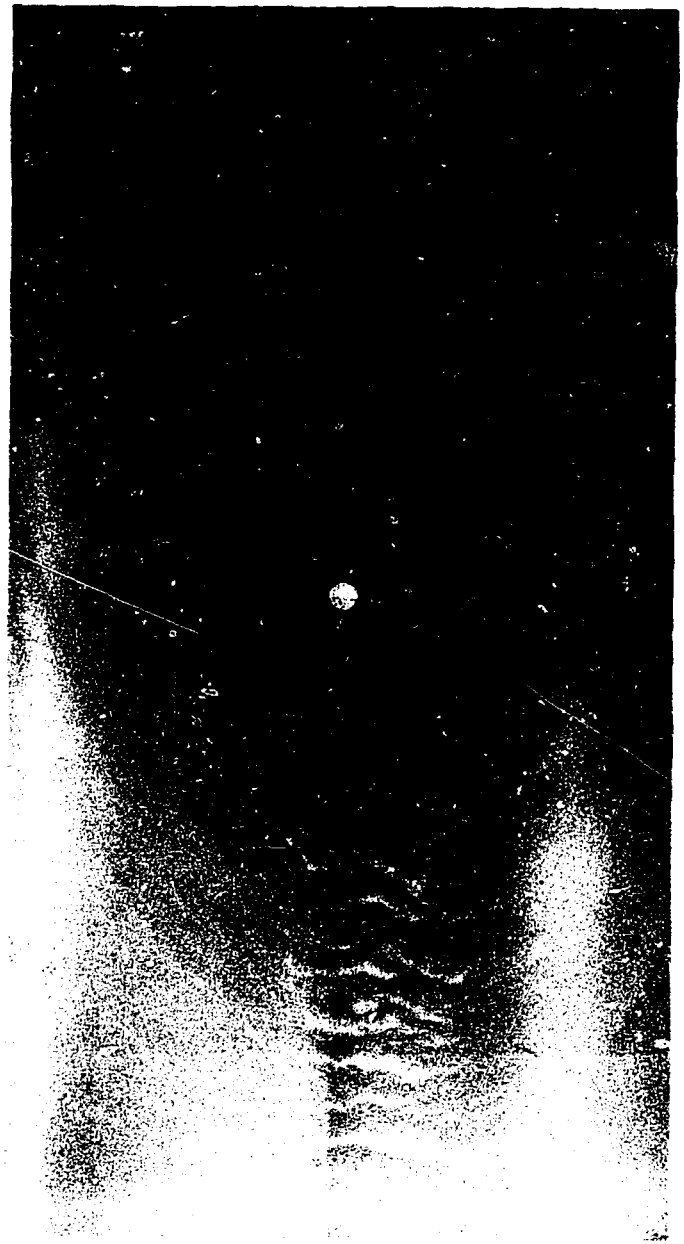
OXYGEN CONTENT OF 178 mm (7-INCH)-DIAMETER INGOTS MELTED USING REAGENT GRADE CaF_2-0.5 wt % MgF_2-5.5 wt % Ca AND REAGENT GRADE CaF_2-5.5 wt % Ca SLAG

Slag Composition	Oxygen Top		
	1	2	3
Reagent grade CaF_2-0.5 wt % MgF_2-5.5 wt % Ca	66	64	71
Reagent grade CaF_2-0.5 wt % MgF_2-5.5 wt % Ca	92	46	68
Reagent grade CaF_2-5.5 wt % Ca	75	61	64
Reagent grade CaF_2-4.8 wt % Ca	38	30	32

Figure 9. TYPICAL INGOT APPEARANCE AFTER ESR MELTING IN A REAGENT GRADE CaF_2-5.5 wt % Ca SLAG. INGOT DIAMETER IS 178 mm (7-INCHES).



(A)



(B)

Figure 10. RADIOGRAPH OF A 0.125-INCH-THICK, VERTICAL SLICE FROM A URANIUM-7.5 wt % NIOBIUM-2.5 wt % ZIRCONIUM ALLOY; (A) ESR PROCESSED USING A CAF_2-5.5 wt % Ca METAL SLAG, (B) VAR PROCESSED.

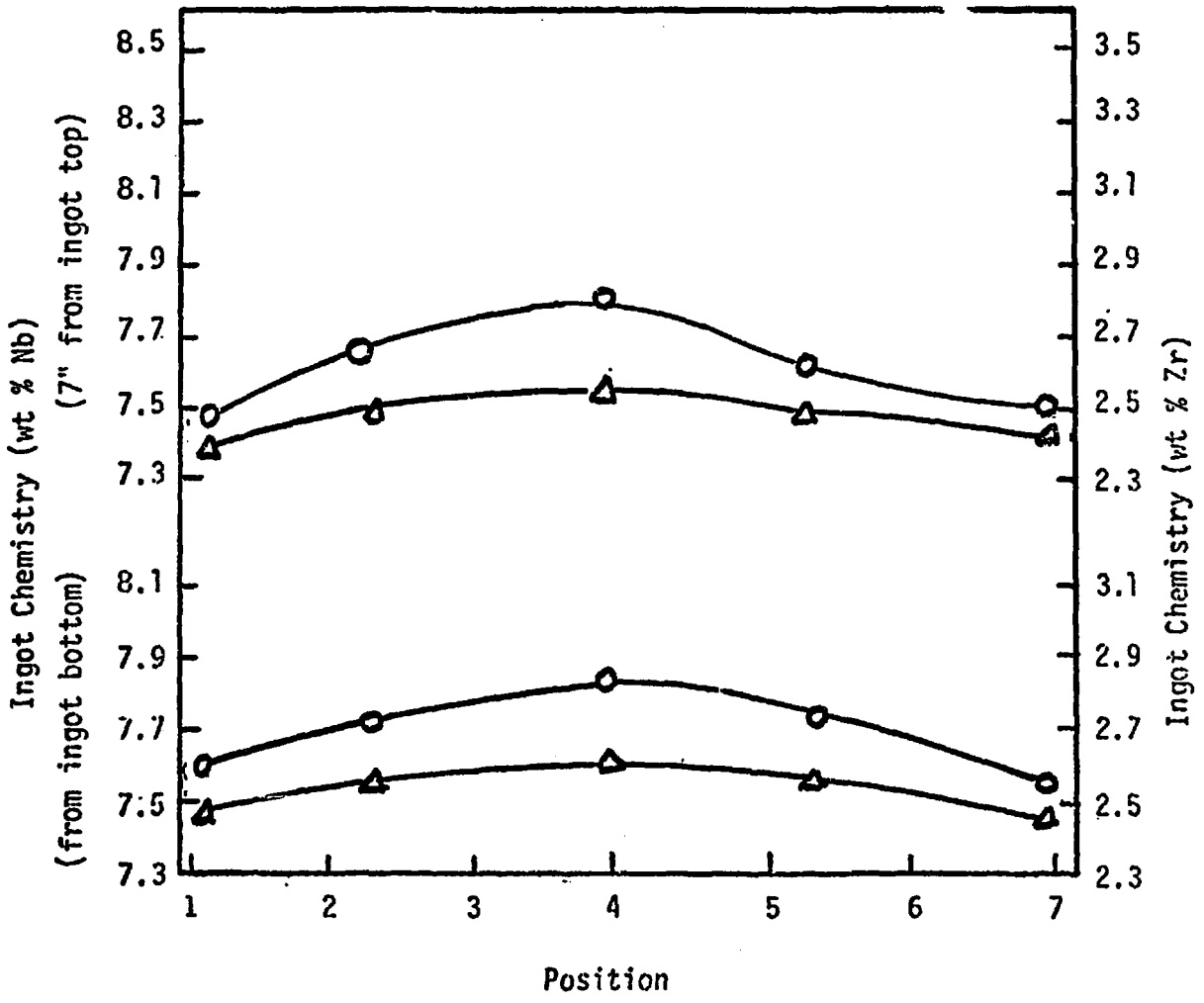


Figure 11. NIOBIUM AND ZIRCONIUM ANALYSES FROM A 7-INCH-DIAMETER ESR MELTED INGOT.

CONCLUSION

ESR melting has been demonstrated to be a viable method of melting a uranium-7.5 wt % niobium-2.5 wt % zirconium alloy. Significant oxygen reductions were achieved in recycling maching turnings which had been a source of contamination. Calcium metal additions to CaF_2 slag were responsible for the oxygen reduction. It was also shown that reagent grade CaF_2 is required to prevent silicon contamination of the melt.

Banding segregation, as observed by radiography, was not eliminated. However, some improvement in the inverse segregation of the niobium to the ingot core was made compared to similar diameter ingots made by the VAR process.

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