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**SLAG REMELT PURIFICATION OF IRRADIATED VANADIUM
ALLOYS**

by

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July 1995

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ABSTRACT

This paper describes theoretical and scoping experimental efforts to investigate the decontamination potential of a slag remelting process for decontaminating irradiated vanadium alloys. Theoretical calculations, using a commercial thermochemical computer code HSC Chemistry, determined the potential slag compositions and slag-vanadium alloy ratios. The experiment determined the removal characteristics of four surrogate transmutation isotopes (Ca, Y - to simulate Sc, Mn, and Ar) from a V-5Ti-5Cr alloy with calcium fluoride slag. An electroslag remelt furnace was used in the experiment to melt and react the constituents. The process achieved about a 90 percent removal of calcium and over 99 percent removal of yttrium. Analyses indicate that about 40 percent of the manganese may have been removed. Argon analyses indicates that 99.3% of the argon was released from the vanadium alloy in the first melt increasing to 99.7% during the second melt.

Powder metallurgy techniques were used to incorporate surrogate transmutation products in the vanadium. A powder mixture was prepared with the following composition: 90 wt % vanadium, 4.7 wt % titanium, 4.7 wt % chromium, 0.35 wt % manganese, 0.35 wt % CaO, and 0.35 wt % Y₂O₃. This mixture was packed into 2.54 cm diameter stainless steel tubes. Argon was introduced into the powder mixture by evacuating and backfilling the stainless steel containers to a pressure of 20 kPa (0.2 atm). The tubes were hot isostatically pressed at 207 MPa (2000 atm) and 1473 K to consolidate the metal.

An electroslag remelt furnace (crucible dimensions: 5.1 cm diameter by 15.2 cm length) was used to process the vanadium electrodes. A measured quantity of calcium fluoride slag, typically 20 to 25 wt %, was placed in the crucible on a layer of vanadium starting material. The furnace was evacuated prior to heating and backfilled with 33 kPa (0.33 atm) helium. An arc was struck and the slag heated until a fully molten slag pool developed in the crucible. Power was then adjusted and electrode feed controlled to obtain good melting with currents of 1200 to 1500 amp (voltages ranged from 20 to 28 volts). The vanadium alloy has higher density than the calcium fluoride slag. Therefore, vanadium alloy droplets melted off of the electrode, passed through the molten calcium fluoride slag, and formed an ingot on the bottom of the crucible below the molten slag. Some of the ingots were melted twice to check for additional purification potential.

Chemical analyses were performed on samples extracted from the slags and ingots. Ingot analyses results are shown below. Values are shown in percent removal of the four targeted elements of the initial compositions.

Removal efficiencies from initial composition.

	Calcium	Yttrium	Manganese	Argon
First melt	94	99.6	42	99.3
Second melt	93	99.8	40	99.7

Slag analyses showed that approximately 0.06 wt % of the vanadium was lost to the slag. Ingot and slag analysis indicated that (0.5 to 10) wt % of the chromium and (15 to 50) wt % of the titanium was lost from the vanadium alloy to the slag.

This work demonstrates that some transmutation isotopes can be removed from vanadium alloys that would be irradiated in a fusion environment. Although this work is preliminary, the data presented here suggest that recycling irradiated alloys by electroslag remelt techniques is promising. This data can be used to further the understanding of activities in irradiated and processed vanadium alloys.

This work was completed in support of the Department of Energy Fusion Safety Program recycling research. The safety of fusion technology extends to not only the machine but also the exposure and hazards to workers maintaining and operating the machine.

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1.0 INTRODUCTION

A study investigating the potential for recycling vanadium alloys irradiated in a fusion power reactor has been conducted and completed. This study was conducted as a preliminary scoping activity to show that appropriately designed fusion reactor materials hold great potential for reduced waste production. This study focused on the V-5 wt % Ti-5 wt % Cr alloy. The processes applied in this investigation are also applicable to the V-4 Ti-4 Cr alloy that has been identified as the preferred alloy for use in a commercial fusion power plant. The V-Ti-Cr alloys have superior strength and high temperature creep resistance under fusion reactor conditions compared to other candidate materials. As a structural material in a fusion power reactor, vanadium will undergo exposure to high energy neutrons inducing significant radioactivity in the material. Recycling the irradiated vanadium would be beneficial since large quantities of vanadium would be needed in the fusion power reactor. For this reason this study was begun, investigating the potential for recycling vanadium alloys irradiated in a fusion reactor environment. This study was composed of three activities: 1) calculation of the induced transmutation products and amounts in a V-5Ti-5Cr alloy under fusion power reactor conditions and identification of candidate treatment processes, 2) calculation of the potential transmutation product removal efficiencies using an equilibrium thermo-chemistry computer code, HSC Chemistry (Outokumpu Research, 1993) and 3) experimental scoping tests to demonstrate the removal efficiencies of a few of the largest accident-dose contributing transmutation products in an electroslag remelt furnace process.

1.1. Starting Material Considerations

Reducing the amount of impurities in the starting material in fusion reactors is significant for many reasons. As shown in Figure 1.1 (Butterworth, 1989), it is important to employ materials with low activation behavior for the safety of the workers operating and maintaining the fusion reactor as well as for the reduction of radioactive waste.

Butterworth and Dolan addressed the impact of impurities in vanadium recycling from a radiological standpoint (Butterworth & Dolan, 1993 and Butterworth, 1991). These researchers generally conclude that lowering impurity levels in the starting vanadium alloy dramatically reduces the number of transmutation isotopes produced during irradiation. The removal of select key impurities prior to irradiation will also reduce the overall difficulty of vanadium recycling since starting material impurity content can significantly affect the activity of irradiated vanadium. Another concern from impurities is the affinity for vanadium to dissolve interstitial elements, i.e., oxygen, carbon, hydrogen, and nitrogen. These elements affect not only initial mechanical properties, but also changes resulting from irradiation. Although exact levels of these impurities needed to meet the requirements for applications in fusion reactors are not completely known, some data are available.

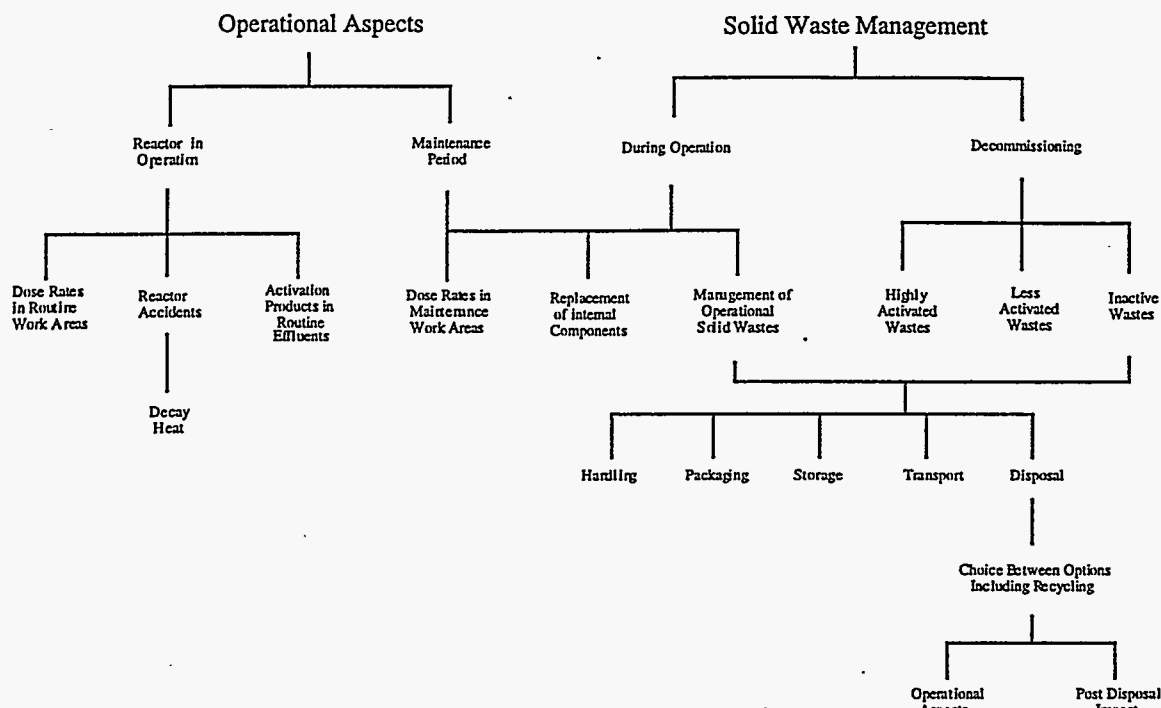


Figure 1.1. Areas of fusion reactor operation that low activation materials would be advantageous (Butterworth, 1989).

Atkins and Rand, 1991, provide a good review of vanadium alloy properties versus impurity content. Hydrogen is the impurity that most influences embrittlement, impact strength, and ductile-to-brittle (DBTT) transition temperatures of vanadium alloys. Alloying content and irradiation, along with hydrogen, synergistically affect these properties. Mattas, et al, 1992 report that a DBTT of less than room temperature may be retainable, after irradiation, if alloying concentrations of titanium and chromium are kept between 3 - 10 wt % and hydrogen impurity is below 30 ppm. Hydrogen can also be removed by vacuum annealing if necessary. The other interstitial impurities are more difficult to remove once they are introduced. Less quantitative information exists regarding acceptable levels of oxygen. Harrod and Gold, 1980, report that increases of dissolved oxygen from 0.005 wt % to 0.22 wt % or nitrogen from 0.005 wt % to 0.11 wt % increased the yield strength of vanadium by three to five times over the temperature range 273-873 K. No mention is made of effects upon ductility. On one hand, Diercks et al, 1986 attribute heat to heat variations in mechanical properties to interstitial contents, but then, Loomis et al, 1986 report that no correlation could be drawn between oxygen, carbon, and nitrogen concentrations and yield stress and total elongation for V-15Cr-5Ti alloys. Takahashi, 1991 shows influences of oxygen, carbon and nitrogen upon the yield stress, hardness and elongation of vanadium. Sharp decreases in elongation, i.e., to values of less than 10 percent, occur as the oxygen and nitrogen levels are increased to above 0.4 and 0.2 wt %, respectively. Increases in carbon to 0.2 wt % decreases elongation. This influence then saturates and elongation remains at about 20 percent with additional increases in carbon. Atkins and Rand also report cases where oxygen has improved creep and creep rupture behavior of vanadium alloys containing Ti and Si.

Fusion power reactor limits for the various structural material interstitial impurities are not yet known precisely. A criteria for recycling could be to try to meet the levels currently obtained by Teledyne Wah Chang using aluminothermic reduction coupled with electron beam melting. The level of these impurities are listed in Table 1.1.

1.2 Recycling Considerations

The recycling effort should start as soon as possible following removal from the reactor and could be conducted as a continuous process. This course of action is recommended for two reasons. First, the vanadium alloy can be brought back into service following irradiation much faster. Also fast recycling will permit removal of certain isotopes relatively easily, before they decay to an isotope that would be more difficult to remove from the alloy. The optimal time period has not yet been established and is dependent upon a number of factors, including the length of time required to move the vanadium from the reactor to the recycling plant. For our work, a period of one year was selected for delay time prior to placement into a recycling plant.

1.3. Candidate Vanadium Recycling Options

A good review of various purification techniques for refractory metals and associated purification is presented by Singh, 1990. Several of these processes and their associated purity levels are listed in Table 1.1. Selecting a candidate purification process is an important step in recycling irradiated materials. The selected possible candidates include the iodide process, the chloride process, electron beam refining, pyrovacuum processing, fused salt processes, and the slag remelt processes.

Table 1.1. Purity levels for vanadium by various purification methods.

Process	Purity w/o	Oxygen ppm	Hydrogen ppm	Nitrogen ppm	Carbon ppm
Teledyne Wah Chang		250	< 5	30	30
Pyrovacuum	99.9	100			
Electro beam zone refining	99.95	235	12	95	NA
Fused salt electrorefining	99.95	900	---	30	20
Fused salt electrorefining	99.99	40	10	7	15
Chlorination	99.95	2000	100	100	---
Iodide process	99.95	40	10	< 5	150
Solid state electrotransport	99.999	< 1	< 1	< 1	< 2

Pyrovacuum melting can sometimes be effective in reducing the levels of oxygen, nitrogen, and hydrogen in refractory metals. Preferential vaporization of some species, such as some oxides, will occur when the concentrations of the gaseous species are low, i.e., a good vacuum is maintained. Singh points out that the ability for refinement depends upon the ratio of the impurity concentrations in the gas phase evaporative mixture to that in the molten metal. Although some reduction can be achieved with vanadium, it has an oxygen ratio in the gas phase to that in the melt of about six at processing temperatures. This ratio, which is lower than those for Nb, Ta, and Hf, means that a greater amount of vanadium metal would be evaporated to achieve a given reduction in oxygen concentrations. In fact, Singh points out that with a reduction value of ten, 10% of the metal would be lost while reducing the oxygen level by one-half. Getters, such as zirconium, may be used to aid in absorbing impurities. Practically, however, the vapor pressure of the impurity should be greater than 10^{-3} Torr at the working temperature and it should exceed the vapor pressure of the metal by more than a factor of ten.

The iodide process is based upon first forming vanadium di-iodide by reaction around 1273 K. This product decomposes when reheated allowing the vanadium to be collected on a filament heated to approximately 1473 K. This is one of the few, or perhaps only, process that could reduce nitrogen levels besides controlling the levels in the stock material.

Some disadvantages according to Rostoker, 1958, appear to be: 1) the process is a batch method employing only small quantities of material (the largest ever processed was two pounds), 2) the reaction forming the VI_2 is slow, and 3) the product formed on the hot filament by decomposition of VI_2 and recirculating iodine was small crystals. A more dense product was formed by removing iodine vapor through a vacuum port and controlling filament temperature. The advantage of this process lies in the selective distillation of each element. Very pure vanadium can be obtained by fractional distillation of iodide. Selective distillation of specific key impurities could also be accomplished to aid the recycling effort.

The chlorination process, which also used vapor distillation for purification, has some advantages and disadvantages in relation to recycling irradiated material. The process has been used to recover other elements, including some in large quantities, e.g., copper, magnesium, etc. The dissociation temperature of the vanadium chlorides is low, less than 773 K (Morgan, Schad, Zakak, 1978). A disadvantage, however, is that an oxychloride, $VOCl_3$, forms and distills along with other vanadium chlorides. Oxygen cannot therefore be effectively removed by this process.

The review of the solid state electrotransport process by Singh shows that ultra high purity levels (< 2 ppm) can be obtained with this method. The quantities produced are small, however, making this method useful merely for the production of material for research purposes.

The purity levels obtained from the fused salt methods above, as reported by Singh, were for one electrolysis. Other investigators (Singh, 1990), using a double-refinement process achieved much purer material. He also mentioned that the fused salt electrolyses process was particularly useful for vanadium, due to the high volatility of this metal which presents a problem with pyrovacuum processing.

Several methods of remelting vanadium scrap have been proposed by (Butterworth, 1991). These have included vacuum arc melting, non-consumable electrode arc melting, electron beam melting, plasma arc melting, electroslag melting, and inductoslag melting. All of these methods utilizing a vacuum environment would lose substantial vanadium due to volatilization as identified by the previous work described for pyrovacuum treatments. The latter two methods, however, have the potential of reducing the loss of vanadium while removing impurities due to the protection imparted by the slag covering the molten material. Electroslag remelting is the current method used to produce the purest available large ingots of both alloy steels and nickel-base alloys (National Materials Advisory Board, 1976). This method produces cleaner material than the vacuum induction melt-vacuum arc remelt (VIM-VAR) process. Both austenitic stainless steels and vanadium bearing alloy steels are produced by this method for critical components such as large forging to be used for rotors, pressure bearing components, etc. This process involves melting an electrode droplet by droplet much in the fashion of consumable electrode melting. Each droplet passes through and is protected by a highly reactive slag. Inclusions and impurities are removed before the droplet solidifies on the other electrode. This process is used to produce clean, homogenous, large tonnage ingots.

Vacuum arc melting (VAR) was one of the most widely used methods for metal processing. However, during the past ten years, use of the electroslag remelting process (ESR) has become more common. The inductoslag remelting process (ISR) has also become a point of interest. Most of the work in inductoslag research has been carried out on iron alloys. Some work has been done on metals with similar chemistry to vanadium such as titanium and zirconium. However, no documented cases of processing vanadium in the electroslag and inductoslag processes have been found.

Characterizing waste streams generated by various refining processes is complex. The amount of secondary waste stream that results likely cannot be determined without development and scale-up of specific processes. Simple secondary activities such as producing a vacuum can result in significant volume of secondary waste. All vacuum systems have an exhaust stream that would require cleanup. One would have to consider the number, i.e., the volume, of HEPA filters that become contaminated. Another important aspect is the size and type of containment vessels used for reprocessing. These become waste unless decontaminated. The volume of waste generated by the decontamination process then becomes a factor. For example in the electron beam melting facility illustrated in Dolan and Butterworth, 1994, much of the metallic volatilized species will plate-out on the interior walls of the melting chamber based upon "line of sight" instead

of being trapped in the vacuum system. Some method such as grinding, grit blasting, or chemical dissolution will then be needed to remove radioactive elements such as manganese from the surfaces. Considerations of the amount of waste generated from recycling vanadium would have to consider such things as:

- a) vacuum and filtering requirements
- b) containment vessels: size, materials
- c) decontamination process for facility
- d) recycling through-put rates and temperatures
- e) reagents used in the recycling process

A computerized literature search was completed to determine whether electroslag remelting has ever been applied to the production of vanadium and vanadium alloys. Although no specific references were obtained relative to remelting vanadium, several other abstracts of interest were obtained. Much of the work within the U.S. dates back to the mid 1970s and stems from the U.S. Bureau of Mines. Nafziger, 1976 reviews the development of electroslag remelting. He states the importance of flux selection and mentions the application of electroslag remelting to reactive and refractory metals. More recent references from Russian, Japanese, and Indian authors address the refining of aluminum and titanium alloys, removal of aluminum from chromium, and evaluation of CrMoV steel produced by electroslag remelting. These sources show that some very reactive elements have been processed by electroslag remelting and indicate that activities of the fluxes can be selected such that partitioning of vanadium into the slag can be avoided. One issue addressed in some of the abstracts however was the evaporation of the fluxes. Flux evaporation may be avoidable by using a flux with relatively high melting temperature. The flux melting temperature for vanadium processing should be slightly lower than that of vanadium.

The use of electroslag remelting to remove uranium from cylinders of iron and aluminum has been described by Tatsuhiko, et al., 1987. The use of a flux appears to have an advantage of containing, or limiting volatilization. Losses and dispersion of radioactive isotopes could thereby be contained within the slag compared to any process using vacuum melting or vapor transport for purification. The secondary waste stream would likely be restricted primarily to that of the slag. Regardless of the method(s) used for vanadium purification, there is an overall activity associated with recycling that must be considered. Figure 1.2 shows a schematic of major handling activities associated with vanadium in a fusion reactor system including recycling.

1.4. Electroslag Remelting

Electroslag remelting is the current method used to produce the purest available large ingots of both alloy steels and nickel-base alloys. Both austenitic stainless steels and vanadium bearing alloy steels are produced by this method for critical components such as large

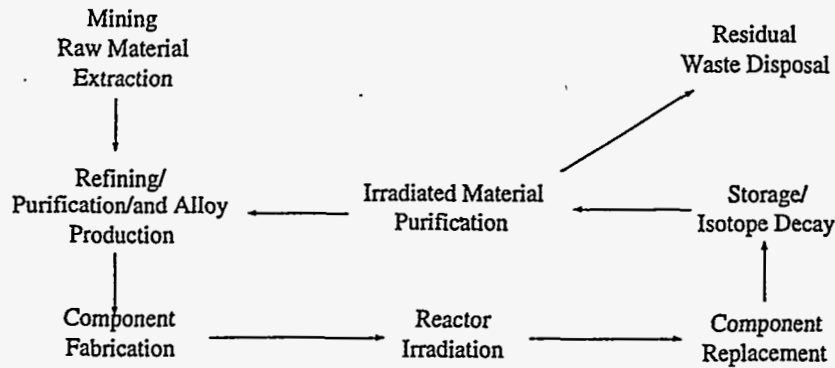


Figure 1.2. Schematic of vanadium in fusion reactor system with recycle.

forging to be used for rotors, pressure bearing components, etc. This process can be used to produce clean, homogeneous, large machinable ingots.

In the electroslag process a solid electrode is polarized with a low voltage-high current power supply. A water cooled crucible serves as the other pole. The connection between the two poles occurs through the slag present in the crucible. The heat produced melts the tip of the electrode droplet by droplet. The electrode melts progressively into a copper crucible similar to the one used in the inductoslag process (Fleming, 1975). As each droplet passes through a highly reactive slag, inclusions and impurities are removed. Refining processes also result from electrochemical reactions that produce ionized species. The migration and deposition of these species can be influenced by polarization potentials across the slag pool (Nafziger et al., 1976). When the electrode's molten metal reaches the bottom of the slag it begins to cool. The cooling metal solidifies at the bottom of the crucible and is pulled out by the starting stub placed there at the initiation of the process (see Figure 1.3). A very critical part of this process is that a thin layer of solid slag coats the inside of the crucible electrically insulating the metal from direct contact with the copper crucible.

1.5. Inductoslag Remelting

Inductoslag remelting is characterized as an induction melting process using an induction radio frequency power supply. The chosen metal melts in a copper crucible with one or more longitudinal slits that prevent attenuation of the field of the surrounding work coil. A thin coat of solid slag forms on the walls of the crucible during the melting process to electrically insulate the molten metal from the copper crucible. This coat of solid slag prevents the molten metal from shorting out the segments of the crucible (Clites, Beall, Nafziger, 1976). A layer of molten slag tops the molten metal within the crucible. This is the slag that will "draw" the transmutation impurities out of the metal. The advantage of using this technique is the capability of being able to melt loose material. Other advantages of this process are that fabrication of a consumable electrode is not needed and the process is carried out under atmospheric pressure.

Melting of the metal in the crucible is set up by placing a starting stub and an initial charge of metal and flux in the crucible. It is important to center the initial charge of metal in the work coil, as shown in Figure 1.4. At the beginning of the run, the starting stub is placed against the lip at the bottom of the crucible (Clites, et. al., 1976). Melting is initiated by applying power to the work coil until the initial charge of the metal and slag has melted. Power is limited at the start of melting to insure melting of some slag before melting the metal (Clites, et. al., 1976). This causes a layer of flux to form against the wall as mentioned before. As soon as a portion of the slag has melted the power is increased, shown in Figure 1.5. The stub is slowly pulled out of the bottom of the crucible as the molten metal solidifies on top of it. As the molten metal travels through the slag and solidifies, impurities can potentially be segregated into the slag.

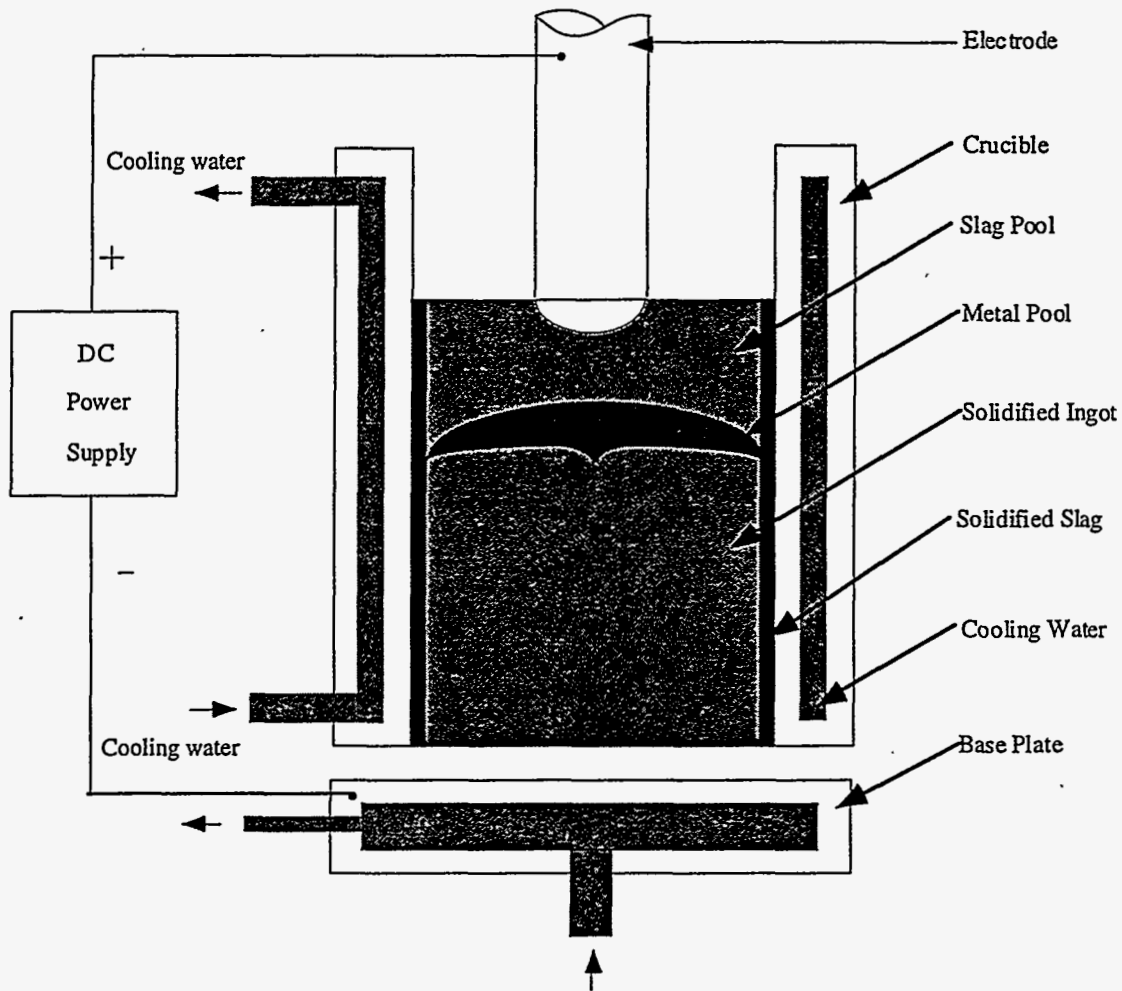


Figure 1.3. A schematic drawing of the electroslag remelting process (side view).

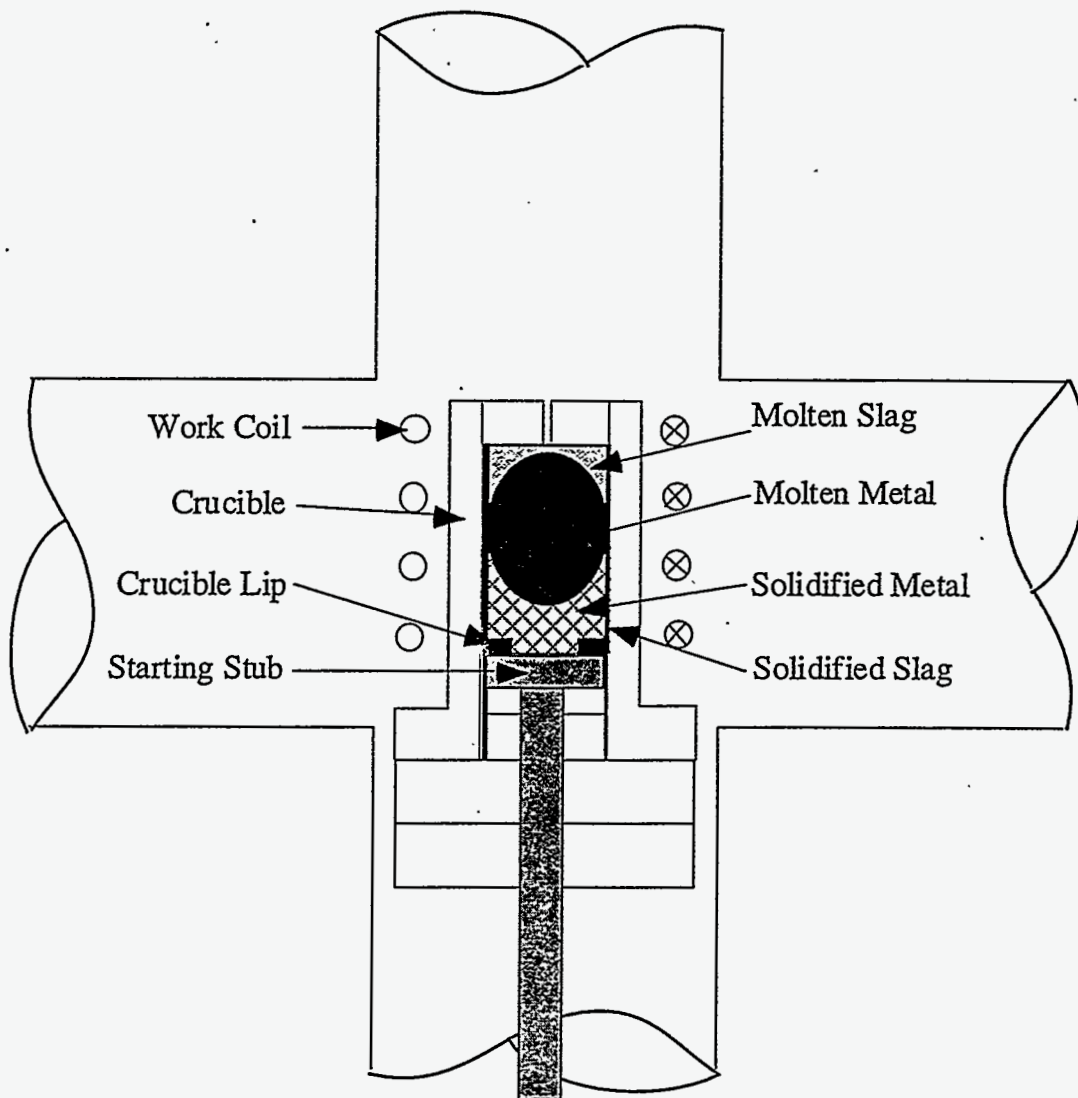


Figure 1.4. A schematic of the inductoslag remelt process.

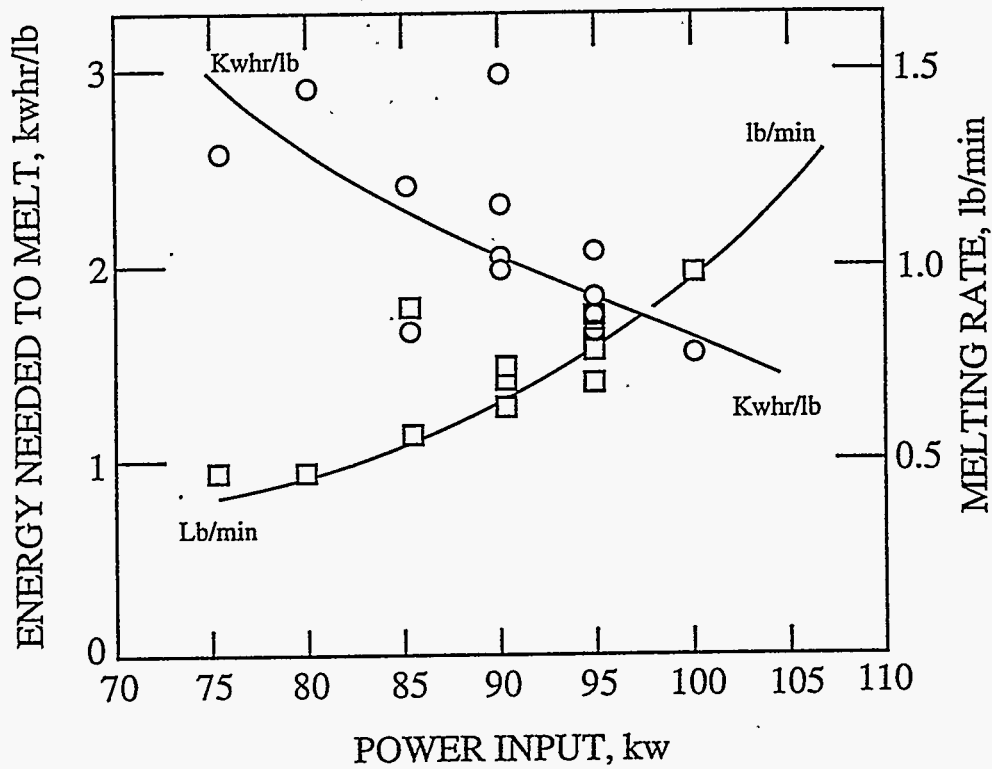


Figure 1.5 . Relationship between power input, melting rate, and energy needed to melt chopped titanium alloy (Clites, et. al., 1976).

square = Melting rate
 circle = Energy needed to melt

2.0 TRANSMUTATION ISOTOPE CONTENT DETERMINATION

The post-irradiation composition and activity of the vanadium alloy will depend upon the pre-irradiation composition and purity. Calculations of the post-irradiation composition and activity have been completed (Forty et al., 1992) by various researchers. These calculations all vary somewhat due to differences in the codes and assumed compositions. These should not impact the recycling effort to a large extent.

The most likely strategy for recycling vanadium alloys would be to allow the alloy to decay for a period of time and then process the alloy in a remote environment. A number of strategies have been proposed on how long the alloy should be stored. The arguments center around allowing the alloy to decay long enough to permit a "hands-on" recycling process. These arguments appear to be academic since most viable recycling methods involve heating the alloy to an elevated temperature and either evaporating radioactive impurities or chemically reacting the impurities. Either way, the recycling process will most likely be a remote "hot-cell" activity regardless of the decay time allowed, even up to 100 years.

Vanadium alloys using around 4 to 5 wt % titanium and around 4 to 5 wt % chromium composition are the leading candidates for use in a fusion power reactor. The currently attainable starting impurity levels are shown in Table 2.1 (Butterworth, 1991). It should be noted that the starting impurities of these alloys depend on a number of variables including feedstock source, process of extraction, and handling. The values reported in Table 2.1 have been obtained from suppliers and represent what is currently available. The same suppliers have indicated that selected lower impurity levels can be achieved for no additional cost. Impurity levels for other selected elements can only be lowered with significantly higher costs.

Vanadium, titanium, and chromium as well as the associated impurities all contribute to the post-irradiation activity. Table 2.3 shows the impurity levels associated with a combination of vanadium, titanium, and chromium (V-5Ti-5Cr) manufactured from the metals shown in Table 2.1. These values were used as the starting material for a REAC*3 calculation. REAC*3 is a computer code developed at Westinghouse Hanford Co. for the purpose of calculating transmutation products resulting from irradiation in a neutron environment (Mann, 1990).

The recycling effort should be started as soon as possible following removal from the reactor. This course of action is recommended for two reasons. First the vanadium alloy can be brought back into service much faster. Also the early removal of certain isotopes may be achieved before they decay into isotopes that are more difficult to remove. The time period is certainly up to debate and is dependent upon a number of factors, including the

Table 2.1. Overall impurity levels for vanadium, titanium, and chromium (ppm by weight)

Element	Van. I	Van II	Van III	Van IV	Ti I	Ti II	Ti III	Cr I
B	0.760	2.100	1.900					
C	39.000			100.00	4.800	45.000	88.000	300.000
N	2.900			60.00	0.120	1.500	0.920	2.200
O	2.800			200.00	3.000	5.000	9.800	1.700
Al		69.000	86.000	140.00	43.000	9.000	18.000	77.000
Sc		0.017	0.007		0.110	0.002	0.037	0.340
Co	0.680	0.120	0.016		0.085	0.096	0.490	14.000
Ni	0.700	3.300	0.640	20.00	11.000	59.000	26.000	3.500
Cu	4.000	0.330	0.130		1.300	29.000	14.000	2.000
Nb	4.900	53.000	20.000	11.00	0.420	0.160	0.310	660.000
Mo	0.034	1.300	55.000	11.00	14.000	1.500	8.100	1.100
Pd	0.002	0.070	0.002		0.130	0.002	0.002	0.002
Ag	0.009	0.010	0.012		0.007	0.012	0.014	0.440
Nd		0.002	0.002		0.002	0.002	0.002	0.003
Sm		0.002	0.002		0.002	0.002	0.002	0.003
Eu		0.002	0.002		0.002	0.002	0.002	0.002
Gd	0.008	0.002	0.002		0.002	0.002	0.002	0.004
Tb	0.001	0.002	0.002		0.002	0.002	0.002	0.001
Dy	0.002	0.002	0.002		0.002	0.002	0.002	0.004
Ho	0.080	0.002	0.002		0.002	0.002	0.002	0.001
Er	0.003	0.002	0.002		0.002	0.002	0.002	0.004
Tm		0.002	0.002		0.002	0.002	0.002	0.001
Lu	0.001							
Hf	0.002	1.300	0.032		0.002	0.002	0.080	0.014
Os		0.002	0.002		0.002	0.002	0.002	0.002
Ir		0.002	0.002		0.002	0.002	0.002	0.002
Pt		0.002	0.002		0.002	0.002	0.002	0.008
Pb		0.005	0.010		0.120	0.110	0.120	0.520
Bi		0.002	0.002		0.004	0.004	0.002	0.002
Fe				100.00				
S				10.00				
P				30.00				
Si				400.00				

- Vanadium I "pure grade", Metallwerk Plansee GmbH
- Vanadium II "very pure" grade, Materials Research Corporation
- Vanadium III 99.8%, sample provided by ECN Petten
- Vanadium IV Spec. Production, Teledyne Wah Chang
- Titanium I 99.9%, sample provided by ECN Petten
- Titanium II Titanium sponge, origin Japan, provided by IMI Titanium
- Titanium III Titanium granules supplied by Deeside Titanium Ltd.
- Chromium I 99.995%, sample supplied by ECN Petten

length of time required to move the vanadium from the reactor to the recycling plant. For this reason a period of one year seems reasonable for placement into a recycling plant. Table 2.4 shows the results of a REAC*3 calculation. The calculation represents the transmutation products present versus time in a V-5Ti-5Cr alloy using starting impurity levels shown in Table 2.3.

Table 2.2. Percent activity contribution properties of vanadium, titanium, and chromium verses allowed decay time (no impurities)

Titanium						
	Shut-down	5 minutes	4 days	1 year	100 years	10 ⁵ years
Sc-48	34.9	39.7	38.8			
Sc-46	19.5	22.2	38.8	26.5		
Sc-47	17.7	20.1	16.6			
Ca-45	12.4	14.1	25.0	73.2		
H-3					71.9	
Ar-42					12.8	
K-42					12.8	
Ar-39					2.5	
Ca-41						100
Vanadium						
	Shut-down	5 minutes	4 days	1 year	100 years	10 ⁵ years
V-52	91.8	85.2				
Ti-51	4.5	5.9				
Sc-48	1.9	4.8	26.5			
Sc-47	0.5	1.2	13.2			
V-49			30.4	95.5		
Cr-51			28.9			
H-3				4.4	100.0	
Ca-41						99.6
Chromium						
	Shut-down	5 minutes	4 days	1 year	100 years	10 ⁵ years
Cr-51	75.8	87.8	96.5	0.7		
V-52	19.5	8.5				
V-49	2.5	2.9	3.5	98.9		
V-53	1.2					
Mn-54				0.1		
H-3					100	
Mn-53						100

There are three primary considerations when evaluating the radioactivity of a particular material. From an accident safety point of view, dose to the most exposed individual is important (there are several types of dose ranging from the dose due to the plume passage only to the dose including ingestion assuming a person grows and eats all his or her food on the site boundary), as well as the decay heat from a particular material. From a maintenance point of view, contact dose is important. 10CFR61 gives guidance for waste disposal. The dominant criterion in waste disposal relates to the dose to the "intruder" 500 years after shutdown. In this study, we concentrated on isotopes that are important in

accident safety, although sometimes the isotopes significant in accident safety are also significant when evaluating contact dose (such as Sc isotopes). Sc, Ca, Mn, and Ar have been identified in various studies as significant for accident dose (Butterworth, et. al, 1993, McCarthy, et. al, 1994). The version of the REAC*3 code used in this study does not include a calculation for argon. Argon is tracked in other codes used for the same purpose and is shown to be significant in accident-dose contribution (Forty et al., 1992).

Table 2.3. Starting impurity levels (ppm by weight) of a V-5Ti-5Cr alloy used to calculate values in Table 2.4.

Element	V(IV)Ti(I)Cr	V(IV)Ti(II)Cr	V(IV)Ti(III)Cr
B	0.0	0.0	0.0
C	105.2	107.3	109.4
N	54.1	54.19	54.2
O	180.2	180.3	180.6
Al	132.0	130.3	130.8
Sc	0.02	0.017	0.02
Co	0.03	0.03	0.03
Ni	18.7	21.1	19.5
Cu	0.17	1.6	0.8
Nb	0.1	0.1	0.1
Mo	10.0	10.0	10.0
Pd	0.007	0.0	0.0
Ag	0.02	0.02	0.02
Hf	0.001	0.001	0.005
Pt	0.001	0.001	0.001
Pb	0.03	0.03	0.03
Fe	90.0	90.0	90.0
S	9.0	9.0	9.0
P	27.0	27.0	27.0
Si	360.0	360.0	360.0

V(IV)Ti(I)Cr Alloy of Vanadium IV, Titanium I, and Chromium from Table 2.1

V(IV)Ti(II)Cr Alloy of Vanadium IV, Titanium II, and Chromium from Table 2.1

V(IV)Ti(III)Cr Alloy of Vanadium IV, Titanium III, and Chromium from Table 2.1

The most significant point to draw from this data and other data similar to it is that the recycling method chosen must be able to remove a number of various elemental species. The number of impurities to be removed decreases with cooling time but this does not always mean that the recycling effort will be any easier. Processing steps producing fine particles or vapors may allow other isotopes to escape from these sources and increase the dose contributions. The recycling method should be capable of modification if other unanticipated impurities needing removal are found in the irradiated material. The recycling process will have to be adaptable in order to accommodate such transmutation impurities.

Table 2.4. Contact dose rate (R/hr) calculated with REAC*3 (Impurities from Table 2.3).

At Shutdown		1 year		10 years	
Element	R/hr/cm ³	Element	R/hr/cm ³	Element	R/hr/cm ³
V	1.52E+02	Sc	7.25E-02	Nb	1.27E-07
Sc	2.70E+01	Co	6.76E-04	Ag	7.38E-08
Ti	6.69E+00	Mn	4.13E-04	Al	4.36E-08
Cr	2.77E-01	Cr	2.80E-05	Mo	2.81E-08
Al	1.26E-01	Ag	3.57E-06	Co	8.86E-10
Na	7.24E-02	Y	6.54E-07	Hf	3.49E-12
N	3.22E-02	Nb	2.84E-07	Pt	4.70E-14
Ca	2.03E-02	Fe	1.66E-07	Ni	1.20E-14
Mg	1.27E-02	Zr	7.05E-08	Ir	5.00E-15
Mn	7.55E-03	Al	4.36E-08	V	4.00E-15
Co	5.81E-03	Mo	2.86E-08	Pb	7.21E-16
Mo	1.16E-03	Rh	3.66E-09	Lu	5.28E-22
Tc	4.45E-04	Hf	3.05E-10	Mn	3.20E-38
Ni	2.00E-04	Ca	6.14E-11	Pd	0.00E+00
P	1.88E-04	V	2.87E-11	Fe	0.00E+00
Nb	8.31E-05	Lu	8.84E-12	H	0.00E+00
Fe	6.12E-05	Hg	2.56E-12	C	0.00E+00
C	5.22E-05	Ru	1.72E-12	P	0.00E+00
Cu	4.07E-05	Tl	1.98E-13	Si	0.00E+00
Ag	1.88E-05	Pt	1.86E-13	Be	0.00E+00
Y	1.01E-05	Ir	1.03E-13	Zr	0.00E+00
Zr	6.32E-06	Pd	2.40E-14	Os	0.00E+00
B	5.33E-06	Ni	1.20E-14	Bi	0.00E+00
Pb	5.07E-06	Pb	7.21E-16	Ti	0.00E+00
Si	2.86E-06	Os	5.45E-17	Cr	0.00E+00
Pd	5.42E-07	S	0.00E+00	Y	0.00E+00
K	2.25E-07	Be	0.00E+00	Cd	0.00E+00
Hf	1.95E-07	P	0.00E+00	Zn	0.00E+00
S	1.48E-07	Si	0.00E+00	Cl	0.00E+00
Rh	2.71E-08	H	0.00E+00	S	0.00E+00
Tl	4.12E-09	C	0.00E+00	O	0.00E+00
O	3.20E-09	Cl	0.00E+00	N	0.00E+00
Ru	1.23E-09	Zn	0.00E+00	Au	0.00E+00
Pt	6.01E-10	Cd	0.00E+00	Cu	0.00E+00
Hg	5.99E-10	Ti	0.00E+00	Tl	0.00E+00
Lu	8.30E-11	F	0.00E+00	Hg	0.00E+00
Au	6.19E-11	Bi	0.00E+00	B	0.00E+00
Yb	4.53E-12	Au	0.00E+00	Ru	0.00E+00
Ir	3.38E-12	Na	0.00E+00	Ca	0.00E+00
Os	6.12E-17	Li	0.00E+00	Ta	0.00E+00
Be	0.00E+00	K	0.00E+00	Mg	0.00E+00
H	0.00E+00	He	0.00E+00	Na	0.00E+00
Zn	0.00E+00	Yb	0.00E+00	Li	0.00E+00
Cl	0.00E+00	Mg	0.00E+00	K	0.00E+00
Ta	0.00E+00	B	0.00E+00	F	0.00E+00
Cd	0.00E+00	Tc	0.00E+00	Sc	0.00E+00
Bi	0.00E+00	O	0.00E+00	Yb	0.00E+00
F	0.00E+00	Cu	0.00E+00	He	0.00E+00
total	1.86E+02	total	7.37E-02	total	2.73E-07

3.0 ESTIMATION OF IMPURITY REMOVAL EFFICIENCY AND SLAG COMPOSITION

3.1. Optimum Physical Properties of Slags

The slag used in both the inductoslag and electroslag remelting processes must have a composition specific to the metal being recycled. Observations of various slags have provided convincing evidence that physiochemical properties of the slags are of prime importance in establishing successful inductoslag melting processes. Knowledge of the thermodynamic properties of molten slags is also of importance. Optimum properties of an ideal slag include:

- (1) the liquid temperature of the slag should be slightly lower than of the metal to be melted,
- (2) the density of the slag must be less than that of the metal at its melting point,
- (3) the electrical conductivity of the slag should be as low as possible for economical operation,
- (4) the heat of fusion of the slag should be low enough for easy melting,
- (5) the thermal conductivity should be low to provide an insulating cap on the ingot,
- (6) the viscosity should be sufficiently low to promote effective stirring for gas removal at the slag-gas interface, yet high enough to increase metal droplet exposure for maximum refining,
- (7) the slag should possess a low vapor pressure at the processing temperature,
- (8) the slag should possess as high a surface tension as possible,
- (9) the slag should possess a relatively large solidification range, to insure that the ingot surface is completely covered,
- (10) the slag should be stable at high temperatures and be compatible with the metal to be melted at such high temperatures,
- (11) the primary slag phase should possess a melting point higher than that of the metal to permit solid slag skin to form between the ingot and mold during melting. The skin is responsible for smooth, workable ingot surfaces following processing.

Reactions that lead to refining, contamination, or loss of unwanted elements can be classified as mechanical (inclusion floatation), chemical, and/or electrochemical (National Materials Advisory Board, 1976). A schematic of the possible reactions and possible reaction sites is shown in Figure 3.1 taken after Nafziger et al. 1976 with modifications.

3.2. Slag Systems

Most of the investigations dealing with slags have been in search of finding a slag satisfying as many of the items in the aforementioned list. It has been suggested that

halides are the most suitable materials for inductoslag and electroslag slags. Borides, carbides, and nitrides are not used because they melt at temperatures too high for practical use or decompose at temperatures greater than 1273 K (Nafziger, Lincoln, & Riazance, 1976). Alkali and transition metal halides as well as most chlorides, bromides, and iodides are unusable because their vapor pressures are high. They are also unstable at the temperatures and pressures of interest. Therefore, the materials are limited to alkaline-earth metals and lanthanon (rare earth plus Yttrium) fluorides. Yet, thermochemical calculations show that these compounds will not react with the titanium in Table 3.1 (Nafziger, Lincoln, & Riazance, 1976).

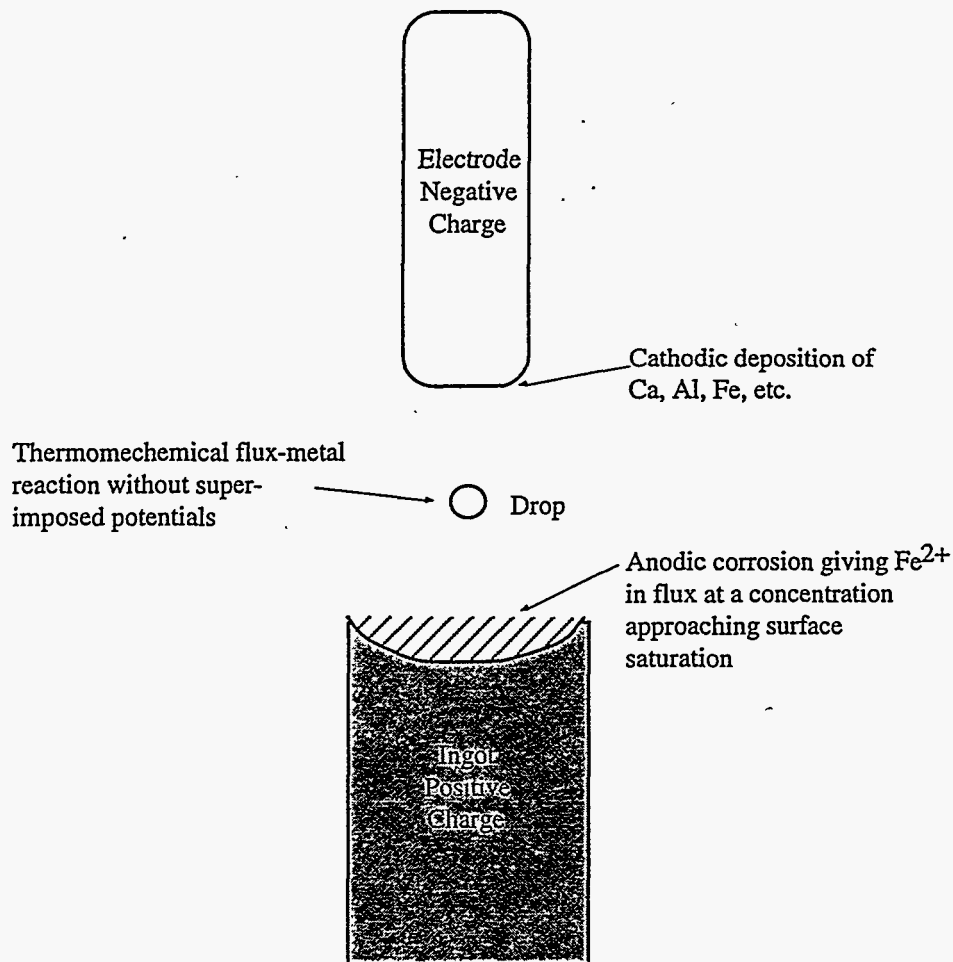


Figure 3.1. Schematic of purifying reactions expected in electroslag remelt processes.

To create a slag specific to vanadium, investigations were carried out on the results from titanium remelting. The reason, as mentioned before, is that vanadium's chemistry is very closely related to titanium's. The first step to identifying an appropriate slag was to analyze available literature data for important physical properties of some candidate fluoride slag compounds as well as representative reactive metals (Table 3.2). High densities presented in Table 3.2 were also studied. Note that all the listed compositions possess melting points below that of the reactive metals listed.

Table 3.2. Selected properties of materials for electroslag (and inductoslag) melting¹

Material	mp, °C	bp, °C	ΔH_{fusion} kcal / mole ⁻¹	ΔG° at 2,000 K, kcal / mole ⁻¹	Vapor Pressure at 2,000 K, (log. atm)	Electrical Conductivity ohm ⁻¹ cm ⁻¹	Viscosity Poises	Thermal conductivity 10 ⁻³ cal sec ⁻¹ cm ⁻¹ 10C ⁻¹
MgF ₂	1,246	2,227 (10)	13.9 (10)	-172 (5)	-1.66 (6)	NA	NA	NA
CaF ₂	1,423	-2,500 (9)	6.8 (10)	-210 (5)	-2.41 (6)	6.39 at 1,527°C (3)	0.058 at 1,600° C (1)	24 (2)
SrF ₂	1,462	2,477 (10)	4.3 (10)	-210 (5)	-2.27 (6)	NA	NA	NA
BaF ₂	1,346	2,200 (10)	3.0 (10)	-214 (5)	-1.61 (6)	NA	NA	27 (2)
YF ₃	1,149	2,227 (4)	13.0 (4)	-300 (5)	NA	NA	NA	NA
LaF ₃	1,487	2,327 (4)	14.5	-315 (5)	-2.40 (6)	3.36 at 1,650°C (8)	NA	NA
Titanium	1,675 (9)	3,285 (6)	4.5 (6)	NAP	-3.92 (6)	NA	NA	NA
Zirconium	1,815 (7)	4,400 (6)	4.6(6)	NAP	-9.34 (6)	NA	NA	NA
Vanadium	1,910 (7)	-3,350 (6)	NA	NAP	-6.36 (6)	NA	0.058 at 1,527° C (7)	24 (2)

NA = not available

NAP = not applicable

¹ Italicized numbers in parentheses refer to references below

1. Bacon, Mitchell, and Nixhizaki, 1972
2. Ballard, Combes, and McCarthy, 1952
3. Davies, and Wright, 1970
4. Gibson, Miller, Kennedy, and Renstorff, 1959
5. Glassner, 1957
6. Kubaschewski, Evans, and Alcock, 1968
7. Maurakh, 1964
8. Mitchell, 1969
9. Weast, 1966
10. Wicks, and Block, 1963

Table 3.1. Standard free energies of reaction at 2000 K.

Slag () and metal []	Calculated ΔG° , kcal		
	n = 2	n = 3	n = 4
$n/2 (\text{MgF}_2) + [\text{Ti}] = (\text{TiF}_n) = n/2 [\text{Mg}]$	+ 11	+ 16	+ 43
$n/2 (\text{CaF}_2) + [\text{Ti}] = (\text{TiF}_n) = n/2 [\text{Ca}]$	+ 46	+ 68	+ 113
$n/2 (\text{SrF}_2) + [\text{Ti}] = (\text{TiF}_n) = n/2 [\text{Sr}]$	+ 42	+ 62	+ 105
$n/2 (\text{BaF}_2) + [\text{Ti}] = (\text{TiF}_n) = n/2 [\text{Ba}]$	+ 54	+ 80	+ 129
$n/2 (\text{YF}_3) + [\text{Ti}] = (\text{TiF}_n) = n/2 [\text{Y}]$	+ 17	+ 24	+ 55
$n/2 (\text{LaF}_3) + [\text{Ti}] = (\text{TiF}_n) = n/2 [\text{La}]$	+ 36	+ 35	+ 69
$n/2 (\text{CaCl}_2) + [\text{Ti}] = (\text{TiCl}_n) = n/2 [\text{Ca}]$	+ 56	+ 96	+ 128

(Glassner, 1957), (Stull & Prophet, 1971), (Wicks & Block, 1963)

This is also true of the high-temperature densities with the exception of LaF_3 , therefore this slag is unsuitable for titanium remelting and predictably for vanadium remelting also. YF_3 systems can only be used if the YF_3 content remains less than 40 wt %. YF_3 systems are preferred over the LaF_3 systems because of better electroconductivity. Overall, CaF_2 systems are still the most preferred slag system. Nevertheless, researchers concluded that no single slag composition is ideal when all the parameters are considered (Nafziger, Beall, Ausmus, & Dunham, 1976).

Table 3.3. Densities of molten fluorides at or slightly above melting points of reactive metals. (Kirshenbaum, Cahill, & Stokes, 1960 and Maurakh, 1964).

Metal	Titanium	Zirconium	Vanadium
Temperature K	1948	2108	2203-2213
Density (g-cm^{-3}) of-			
Metal	4.11	6.06	5.734
CaF_2	2.417	2.358	2.319
SrF_2	3.33	3.23	3.126
BaF_2	3.824	<3.75	<3.75
MgF_2	2.213	2.133	<2.125
LaF_3	4.462	4.357	4.29

Small amounts of reducing agents have been added to CaF_2 slags to remove oxygen from the molten metal during remelt processing. Relatively volatile constituents were also added to assess if they remove or reduce gaseous impurities. As a result the following slags have been used with titanium.

1. CaF_2 , reagent, acid-grade, native fluorspar
 2. Additions to CaF_2 :
 - 1,3,5 wt % C
 - 2,5 wt % Y
 - 3 wt % Gd
 - 5 wt % K_2TiF_6
 - 5, 7.5, 10, 20, 23, 30, 58, wt % CaCl_2
 - 18.5 wt % SrF_2
 - 4, 12 wt % MgF_2
 - 4 wt % MgF_2 - 50 wt % LaF_3
 - 1 wt % C - 9 wt % MgF_2
 - 20, 52, 75, w/o LaF_3
 3. MgF_2
 4. 80 wt % MgF_2 : 20 wt % LaF_3
 5. LaF_3
 6. BaF_2
- (Nafziger, Beall, Ausmus, & Dunham, 1976)

Extensive testing has shown that approximately half of the tested slag compositions mentioned previously give satisfactory operating conditions and results (Nafziger, et. al., 1976). Degassing was observed in the slags using MgF_2 resulting in loss of slag material.

This is due to the less stable nature of this compound at operating temperatures. LaF_3 tends to become trapped in the metal because of its density. The best operating conditions obtained were with either the acid or reagent grade CaF_2 slag (Nafziger, et. al., 1976).

It has also been determined that the top portion of the CaF_2 slag cap formed after a melt can be reused without affecting impurity concentrations. This is imperative from the economical standpoint of the inductoslag and electros slag processes. Unfortunately, sidewall-flux is not able to be reused because of high contamination (Nafziger, et. al., 1976).

Los Alamos National Laboratory is also performing slag research. They are presently using slags to decontaminate waste streams. Both processes use the slags to pull out unwanted impurities to minimize wastes placed in repositories. The investigations carried out on mild carbon steel proved to be the most helpful. Experimental results, showed that the most effective slag was 40% SiO_2 , 40% CaO , and 20% Al_2O_3 . Increased decontamination was further achieved with small additions of NiO and CaF_2 . In addition, the most effective slag basicity was around 1.5 (Joyce et al. 1993).

3.3 Predicted Removal Efficiency and Slag Composition Performance

Chemical thermodynamics as predicted using the HSC Chemistry (Outokumpu, 1993) package was used to determine slag compositions best suited for vanadium alloy purification. The computer code uses equilibrium thermodynamics (Gibbs free energy, enthalpy, and heat capacity) to calculate the most stable phases resulting from a known set of reactants at a chosen temperature. An equilibrium cell operating at 2173 K was used as the model for the slag remelt process. Kinetic effects as well as solution chemistry were not considered. These calculations and exercise yield only trends or approximations in the overall reaction of starting materials and thus provide general guidance toward slag suitability. Solution chemistry and electrochemical reactions are suspected to play an important roll in the overall behavior and interaction between the metal and slag but could not be accurately incorporated into the calculations.

Three slag compositions were identified as having suitable properties with relation to vanadium alloys, CaF_2 , SrF_2 , and BaF_2 . Calculations were performed with an equilibrium cell containing a V-5Ti-5Cr alloy containing 3 wt % each of Mn, Ca, and Y and the candidate slag material (CaF_2 , BaF_2 , or SrF_2).

Table 3.4 is a summary of the equilibrium calculation using CaF_2 slag. The calculation indicates approximately 46% removal of yttrium from the vanadium alloy. All other alloy constituents were predicted to remain in the alloy. The calculation technique does not calculate the behavior of small amounts of materials when in the presence of a large amount of the same species in a different chemical form. Since the amount of CaF_2 slag is

approximately nine times as large as the amount of calcium in the alloy, the computer code estimates of the free calcium are not reliable. We therefore expect calcium behavior to differ from the calculated results and actually be partitioned to the slag.

Table 3.4. Results of HSC Chemistry calculation for CaF₂ slag.

Species	Initial Amount Electrodes	Predicted amount in metal	Predicted amount in slag
V	9.128	100 %	0 % VF ₂ , VF ₃ , VF ₄ , and VF ₅
Ti	0.522	100 %	0 % TiF ₂ and TiF ₃
Cr	0.481	100 %	0 % CrF ₂ , CrF ₃ , and CrF ₄
Y	0.056	54 %	46 % YF ₃
Mn	0.091	100 %	0% MnF ₂ , MnF ₃ , and MnF ₄
Ca	0.125	100 %	0 % CaF ₂
CaF ₂ (slag)	0.952		

Table 3.5 shows the results of the equilibrium calculation using SrF₂ slag. Similar to the CaF₂ slag, the SrF₂ slag is predicted to remove more than 50% of the yttrium from the alloy. Over seventy percent of the calcium is predicted to report to the slag as well.

The BaF₂ slag calculation results are shown in Table 3.6. The calculations show this slag to be the best performing of the three, removing 77% of the calcium and 95% of the yttrium.

CaF₂ was chosen to be the first slag composition attempted for electroslag remelting of vanadium. The primary reason for choosing CaF₂ over BaF₂ or SrF₂ was the large experience with CaF₂ in the electroslag remelting of titanium. We expect that SrF₂ and BaF₂ would provide good results as a slag by themselves or mixed with CaF₂.

Table 3.5. Results of HSC Chemistry calculation for SrF₂ slag.

Species	Initial Amount Electrodes	Predicted amount in metal	Predicted amount in slag
V	9.128	100 %	0 % VF ₂ , VF ₃ , VF ₄ , and VF ₅
Ti	0.522	100 %	0 % TiF ₂ and TiF ₃
Cr	0.481	100 %	0 % CrF ₂ , CrF ₃ , and CrF ₄
Y	0.056	33 %	67 % YF ₃
Mn	0.091	100 %	0% MnF ₂ , MnF ₃ , and MnF ₄
Ca	0.125	28 %	72 % CaF ₂
SrF ₂ (slag)	0.952		

Table 3.6. Results of HSC Chemistry calculation for BaF₂ slag.

Species	Initial Amount Electrodes	Predicted amount in metal	Predicted amount in slag
V	9.619	100 %	0 % VF ₂ , VF ₃ , VF ₄ , and VF ₅
Ti	0.522	100 %	0 % TiF ₂ and TiF ₃
Cr	0.481	100 %	0 % CrF ₂ , CrF ₃ , and CrF ₄
Y	0.056	23 %	77 % YF ₃
Mn	0.091	100 %	0% MnF ₂ , MnF ₃ , and MnF ₄
Ca	0.125	5 %	95 % CaF ₂
BaF ₂ (slag)	1.023		

4.0 TEST APPARATUS

4.1. Sample Fabrication and Preparation

Vanadium samples were fabricated from a mixture of powders (0.35 wt % CaO, 0.35 wt % Mn, 0.35 wt % Y₂O₃ (as a surrogate for Sc), 4.7 wt % Ti, and 4.7 wt % Cr) and dendritic vanadium. This composition was chosen for two reasons. First the vanadium composition (V-5Ti-5Cr) approximates the currently viewed alloy of choice for a commercial size fusion reactor. Secondly, the impurities and amounts were chosen from REAC*3 calculation results shown in Table 2.4. The dendritic vanadium is not a powder but large "crystals" of vanadium made sometime in the mid-1960s from an electrolytic molten salt process by the U. S. Bureau of Mines. This material was used because of its availability. Measured amounts of the dendrites and a master mix of the blended powders were cold-pressed into pellets about 23 mm in diameter and 8.3 mm thick. These pellets were then stacked on top of each other into stainless steel tubes. The tubes were evacuated to approximately 10⁻⁷ torr and back-filled to 20 kPa (0.2 atm.) with welding grade argon. The cans were then HIPped (Hot Isostatically Pressed) at 1473 K at a pressure of 207 MPa (2000 atm.) for two hours. Figure 4.1 shows a photograph of the electrodes prepared from the mixture of the powders and dendrites following removal of the stainless steel cans. The cans were removed by mechanical machining.

4.2 Electroslag Remelt Furnace at U.S. Bureau of Mines

The electroslag remelt furnace used for this study was constructed by the U.S. Bureau of Mines during the late 1960s for the purpose of developing electroslag remelting processes for a range of different alloys and metals including titanium. Figure 4.2 shows a schematic of the furnace used for this study.

4.3 Chemical Analyses

Chemical analyses were conducted at the U.S. Bureau of Mines in Albany, Oregon and at the U.S.G.S. in Reston, Virginia. Analyses were performed on initial electrodes, as-reacted slags, and the resulting vanadium alloy ingots. Chemical analyses consisted of four procedures:

- (a) volumetric wet chemical analyses for titanium and vanadium,
- (b) Ar⁴² analyses for argon content,
- (c) inductive coupled plasma (ICP) combined with a mass spectrometer for yttrium,
- (d) and atomic absorption analyses (NaOH dissolution) for manganese, chromium, and calcium.

Detection limits associated with the analytical instruments used for these analyses are shown in Table 4.1

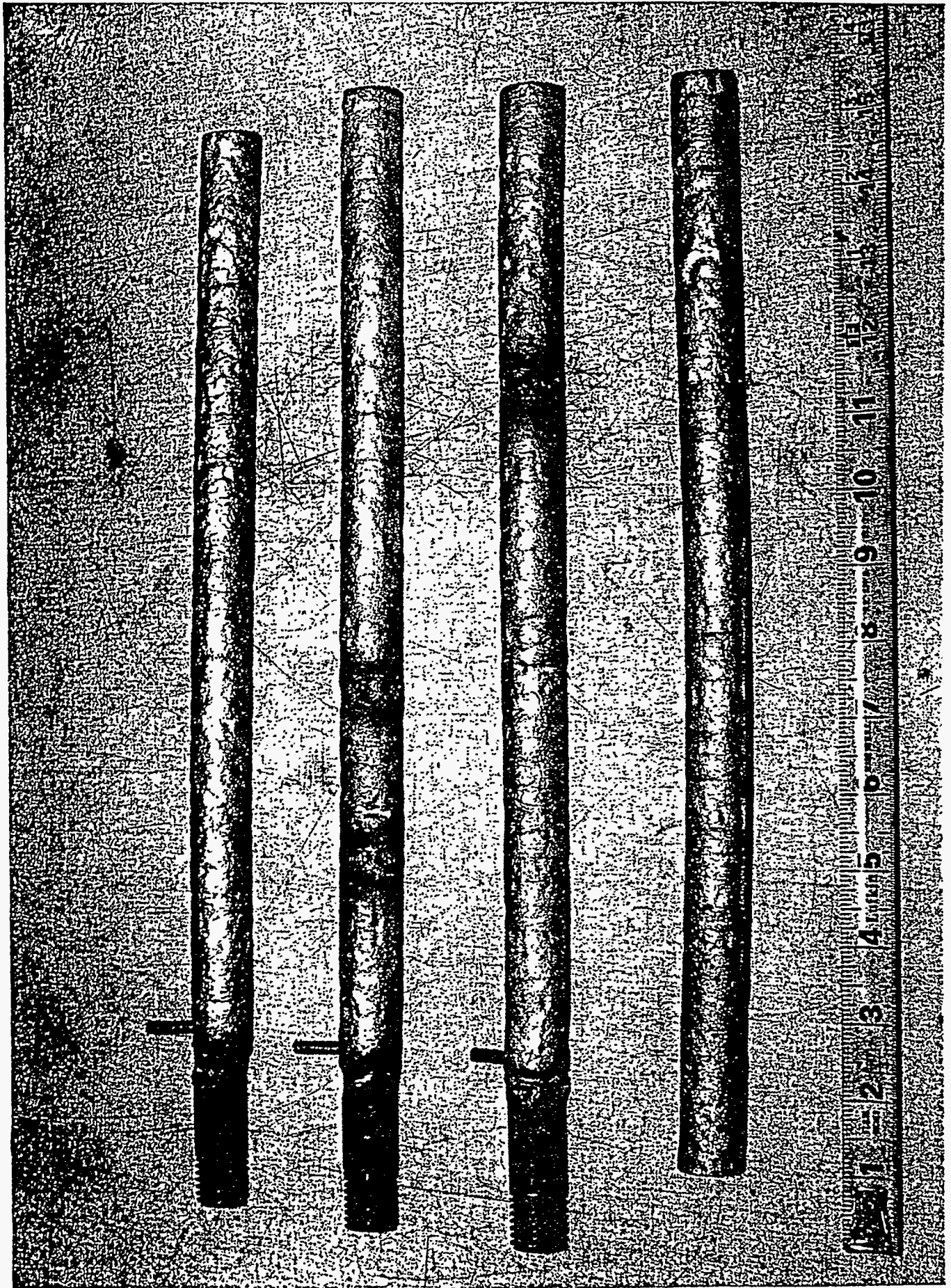


Figure 4.1. Photograph of the vanadium electrodes.

Table 4.1 Detection limits for the analytical methods used for the various elements.

Ca	Cr	Mn	Ti	V	Y	Ar
~1 ppm	~1 ppm	~1 ppm	~0.05 %	~0.02 %	~10 ppm	2 %

The vanadium alloy samples were washed in acetone, alcohol, and deionized water and packaged in aluminum foil prior to analysis. The aluminum foil served to contain the sample, and lower the melting point of the vanadium alloy.

All samples were analyzed on a VG Isotopes, Ltd., Model 1200 B Mass Spectrometer at the U.S. Geological Survey, Reston that was calibrated for argon sensitivity against MMhb-1 (Alexander et al., 1978). Argon was released from the samples in a small volume molybdenum-lined "low blank" tantalum furnace that was attached to an ultra-high vacuum cleanup system. All samples were degassed controlled by a proportional, programmable controller. The furnace and the rear manifold were evacuated as necessary by a turbo molecular pump. Two isolated ion pumps evacuated the front manifold and the mass spectrometer tube. During normal operation, the gas to be analyzed was purified in the rear manifold by a Saes ST707 Zr-V-F getter operated at room temperature. Gas was equilibrated with the front manifold with an empty cold finger (in the rear manifold) chilled with liquid N₂ to remove condensables, and cleaned in the front manifold by a Saes ST101 Al-Zr getter operated at 400°C and a TI(H₂) getter operated at a constant 350°C. An activated charcoal finger submerged in a constant boiling mixture of dry ice and acetone was used to remove gasses with a molecular weight greater than 60 or 80 (primarily noble gases) prior to the admission of the argon dominated gas to the mass spectrometer by expansion. The argon-rich gas was further purified in the mass spectrometer by a second Saes ST101 getter operated at room temperature. Argon isotopes with masses 40 through 36 and CO₂, mass 44, were analyzed as a function of time in five analysis cycles. The peaks and their baselines, were measured as five second integrations in each of the five cycles. After the analysis, the mass spectrometer was evacuated. If necessary, the fraction of gas remaining in the front manifold could be introduced into the mass spectrometer for a replicate "split" analysis.

The isotopic measurements made in the five cycle analysis had baseline values subtracted and then were regressed, to T₀, the time of inlet of the gas to the mass spectrometer, using standard linear regression techniques. The regressed values of the ⁴⁰Ar and ³⁶Ar peaks were used to estimate the argon concentrations of the samples. Statistical estimates of analytical uncertainties of the time zero ⁴⁰Ar peak values were in all cases less than 0.1%. Because the isotopic composition of all samples was atmospheric (⁴⁰Ar/³⁶Ar = 295.5), the ³⁶Ar represents only about 0.338% of the total argon and its uncertainty becomes trivial. The values reported have been corrected for argon contained in the aluminum packaging.

The primary sources of error in the reported values are related to the sensitivity calibration of the mass spectrometer (about 2%), and the uncertainty of the argon content of the aluminum packaging (as much as 0.4% but usually much smaller). These values were

quadratically combined to produce the reported uncertainty estimates. All other sources of error are essentially lost in the "noise" at the resolution reported.

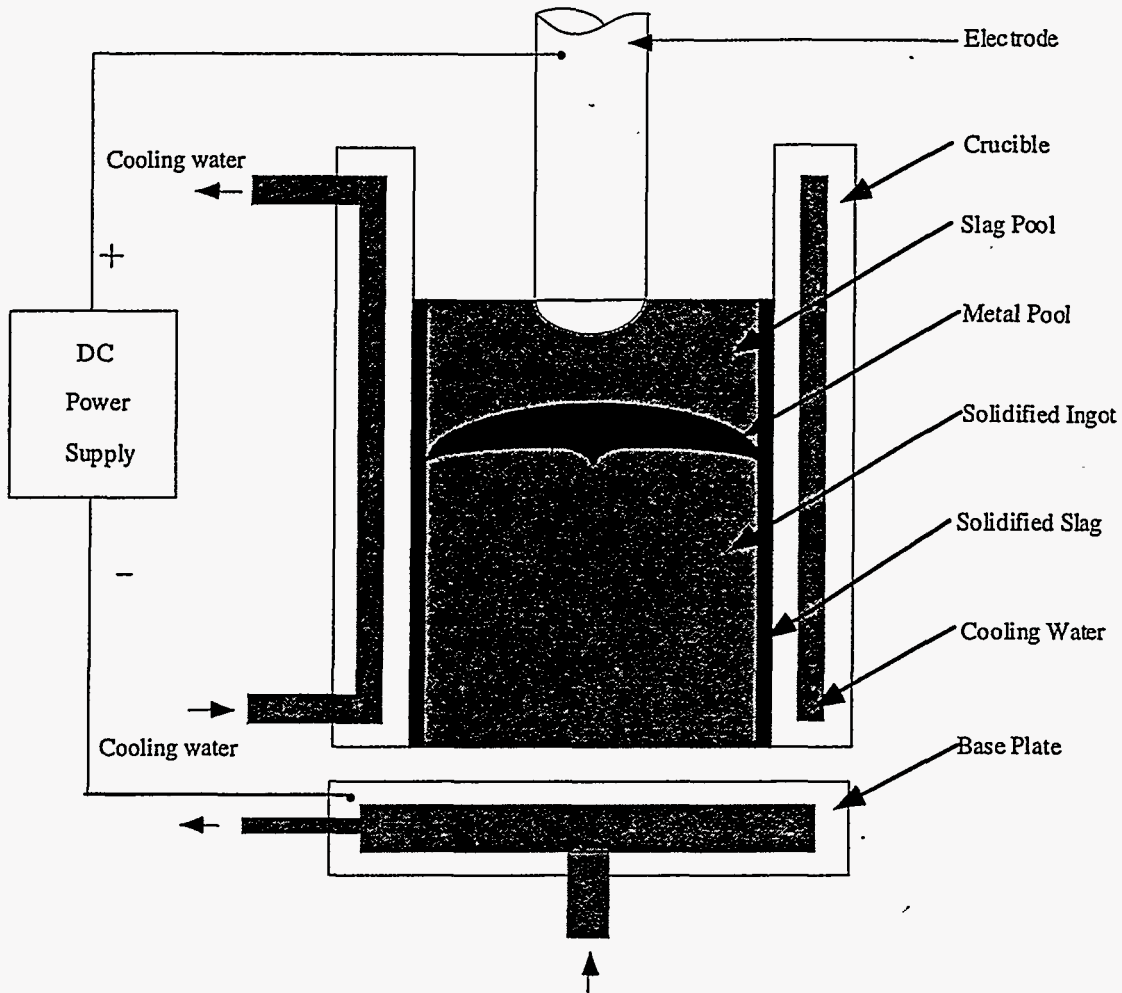


Figure 4.2. A schematic of the electroslag remelt furnace at the Bureau of Mines, Albany.

4.4 Metallographic Examinations.

Metallurgical examinations were conducted at the Idaho National Engineering Laboratory. A scanning electron microscope (SEM) was used to identify regions of interest in the samples and energy dispersive wavelength spectroscopy (EDS) used to give semi-quantitative analyses of metallic constituents. These analyses were completed on an unmelted portion an electrode to show the as-fabricated structure, as well as, the remelted ingots from Electrodes 1 and 4. Samples were prepared metallographically and etched in hydrofluoric acid. Additional samples were simply cut from the ingots and mounted in metallographic mounts but not polished nor etched.

5.0 RESULTS

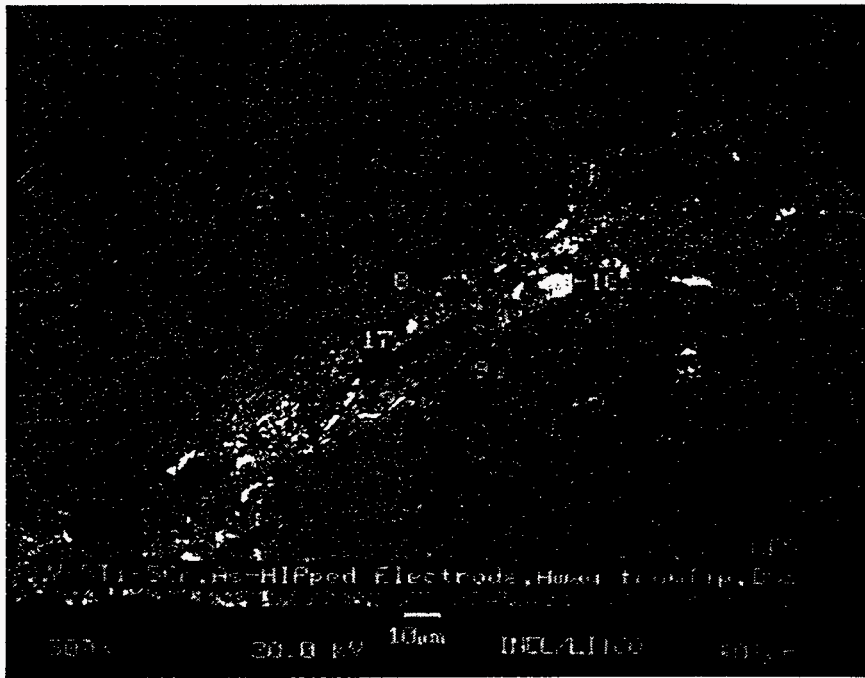
5.1 Sample Fabrication and Preparation

Five vanadium alloy electrodes were fabricated by the HIPping method. Results from a single analysis from each electrode are shown in Table 5.1. The elemental composition of the input mixture is included for comparison. The analytical results for the elements added as fine powders indicate that the distribution was not uniform and that their measurements are significantly lower than the mixed composition. SEM-EDS analyses for titanium and chromium in remelted Electrode 4, shown in Section 5.4, on the other hand, show concentrations corresponding quite well with the mixed composition. We suspect that the elements added as fine powders were not completely alloyed during HIPping and that some of the powder could have been lost during the sampling or preparation for chemical analyses, or that the powder oxides or surface oxides may have prevented the particles from being completely dissolved. The best value to represent initial electrode composition therefore is the composition of the input mixture.

Table 5.1. Measured compositions of the as-fabricated electrodes.

Electrode	Y (wt %)	Mn (wt %)	Ca (wt %)	V (wt %)	Ti (wt %)	Cr (wt %)	O ₂ (wt %)	Ar (ppb)
1	0.053	0.088	0.115	96.420	1.247	1.858	0.220	5746
2	0.089	0.146	0.182	93.248	2.213	3.717	0.199	-
3	0.005	0.184	0.200	89.442	5.449	4.124	0.299	-
4	0.073	0.149	0.173	93.248	2.469	2.862	0.329	2757
5	0.078	0.143	0.162	93.248	3.066	2.927	0.269	-
Average	0.06	0.14	0.17	93.12	2.89	3.10	0.26	-
Input Mixture	0.28	0.35	0.25	89.5	4.71	4.71	0.18	-

An unmelted portion of Electrode 4 was examined with SEM after the remelt operations. SEM micrographs of this as-HIPped material are shown in Figure 5.1. The positions at which EDS spectra were taken are identified by numbers. The results from these standardless EDS analyses are given in Table 5.2. The SEM micrographs show included material within pockets of a pure vanadium matrix. This is what we expected since the dendritic vanadium crystals as shown in Figure 5.2 were quite coarse. The EDS analyses identifies titanium, chromium, yttrium, and iron as being in the agglomerated material in the inter-dendritic regions. Manganese and calcium are not reported, but often elements of low concentration can be masked by other peaks in EDS spectra. The presence of iron likely stems as a contaminant in one of the original powders. It is our expectation that some of the argon back-filled into the mixtures before HIPping was also trapped in such inter-dendritic regions. This is confirmed by the residual amounts of argon found during analysis. These examinations confirm that some of the powder additive were not alloyed and that the electrode material was not homogeneous.



(a)



(b)

Figure 5.1. SEM micrographs of regions in the unmelted portion of Electrode 4. The numbers identify the locations of EDS analyses.

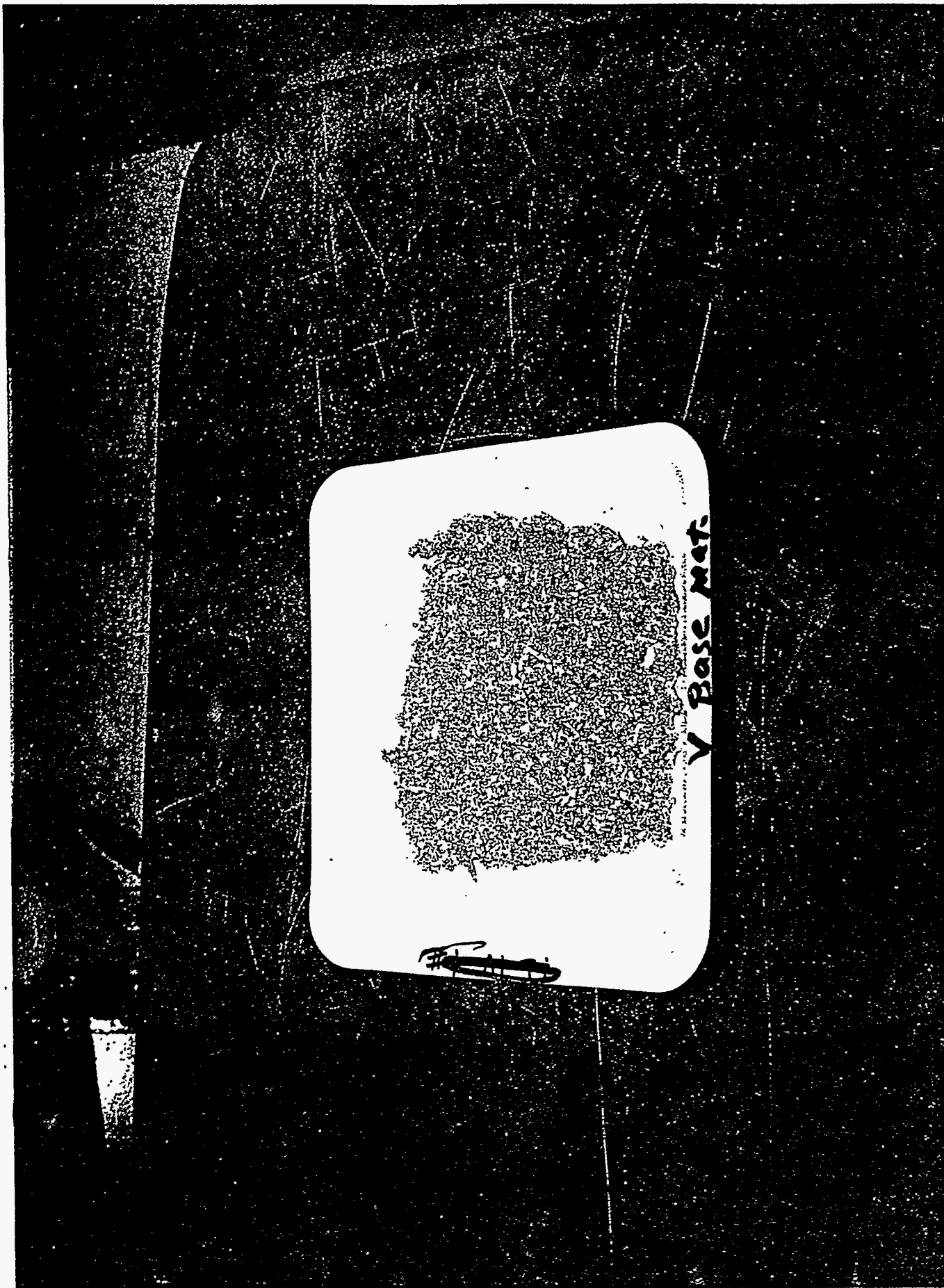


Figure 5.2. Dendritic vanadium used in the fabrication of test electrodes.

Despite this non-uniformity the consolidated electrodes were still adequate for our purpose of scoping studies to evaluate the use of electroslag remelting for vanadium and to demonstrate removal potentials for certain impurities. It is common practice by the U.S. Bureau of Mines to merely use cold pressing to consolidate material for electrodes.

Table 5.2 EDS results from as-HIPped regions of Electrode 4, wt %.

Table 5.2. EDS analysis results from as-HIPped regions of electrode 4.

Analysis #	V (wt %)	Ti (wt %)	Cr (wt %)	Fe (wt %)	Y (wt %)	O (wt %)
7	100	0.0	0.0	0.0	0.0	0.0
8	56.19	29.24	14.57	0.0	0.0	0.0
9	57.83	26.83	15.22	0.12	0.0	0.0
10	100.0	0.0	0.0	0.0	0.0	0.0
11	33.75	32.30	33.73	0.22	0.0	0.0
12	10.04	39.91	49.69	0.36	0.0	0.0
13	1.36	8.83	89.63	0.18	0.0	0.0
14	3.10	34.86	61.71	0.33	0.0	0.0
15	0.00	97.21	2.79	0.0	0.0	0.0
16	0.84	0.60	0.64	0.0	83.08	14.84
17	48.22	36.95	14.68	0.15	0.0	0.0
18	1.42	0.62	0.41	0.0	80.00	17.56

5.2 Electroslag Remelt Furnace at U.S. Bureau of Mines

The electroslag remelt furnace at the U.S. Bureau of Mines performed well. The tests required 1200 to 1500 amps at 28 to 30 volts during electrode feed, i.e., during the melting stage. The tests were all performed with a helium back-pressure of 30 kPa (0.3 atm.) in the chamber except for one test that was completed in a vacuum of approximately 0.13 Pa (1×10^{-3} torr). A photograph of the electroslag remelt furnace used for these tests is shown in Figure 5.3

A typical electroslag remelt experiment consisted of the following steps. The bottom of the furnace crucible was lined with a material with a similar composition to that of the electrode material. This was to prevent direct arcing and damage to the water cooled copper crucible shown in Figure 5.4 One of the HIPped alloy electrodes is shown in Figure 5.5 Dendritic vanadium, shown in Figure 5.2, was used as the starter material during the first test. All of the following tests were conducted using a pad cut from the bottom of the ingot from the previous run. The electrode was positioned to just touch the pad material. The slag material, shown in Figure 5.6, was then poured around the electrode on top of the starter pad. The furnace was closed and evacuated and then re-pressurized to 30 kPa (0.3 atm.) with welding grade helium gas. Welding grade argon gas can also be used, but helium was used because one primary objective of this study was determine the removal efficiency of argon from the vanadium alloy. Power was applied, striking an arc between the vanadium

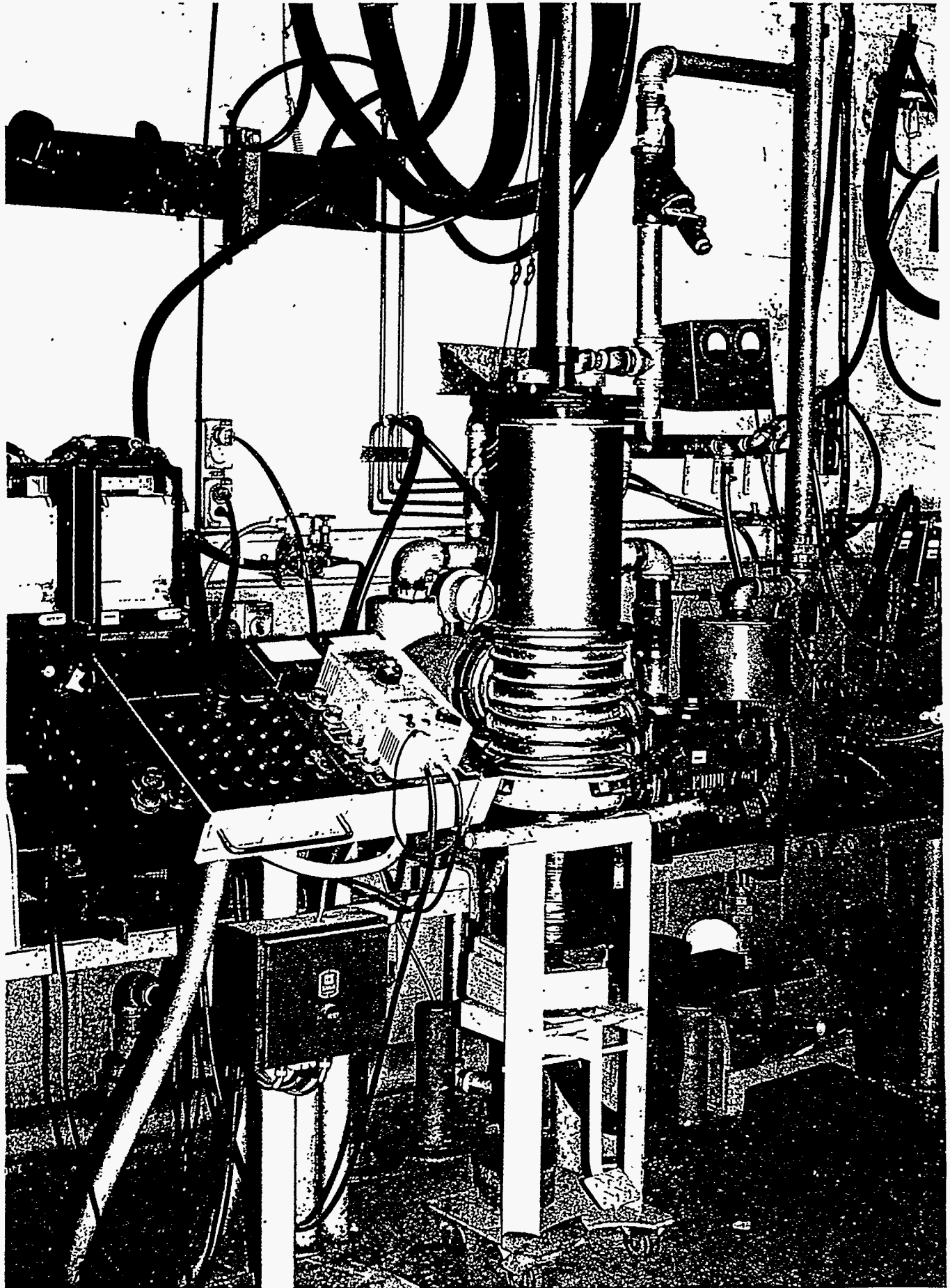


Figure 5.3. Electroslag remelt furnace located at the U.S. Bureau of Mines, Albany, OR.



Figure 5.4. Water cooled copper crucible.

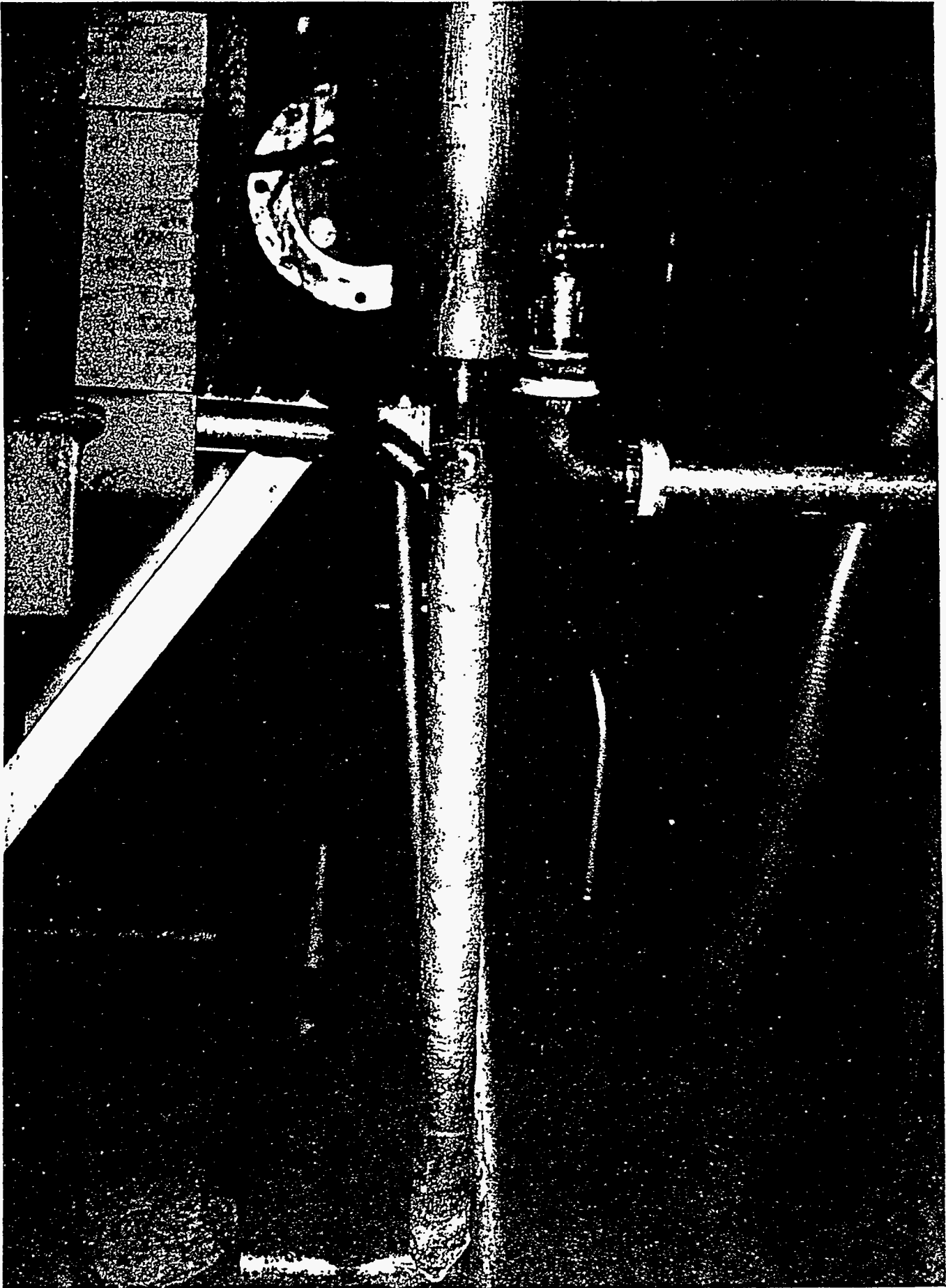


Figure 5.5. Vanadium electrode attached to positive electrode "stinger" assembly.

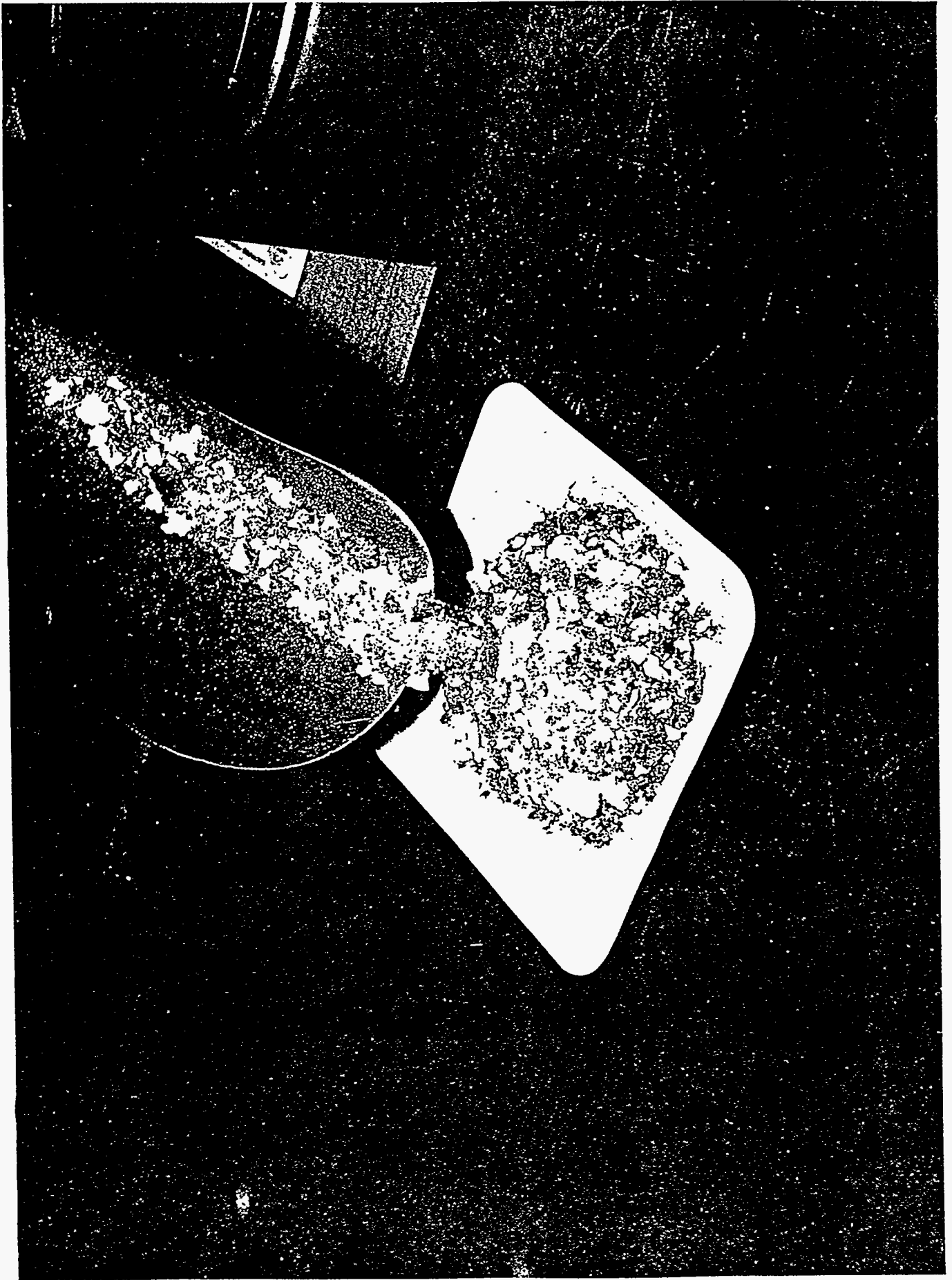


Figure 5.6. Calcium fluoride slag.

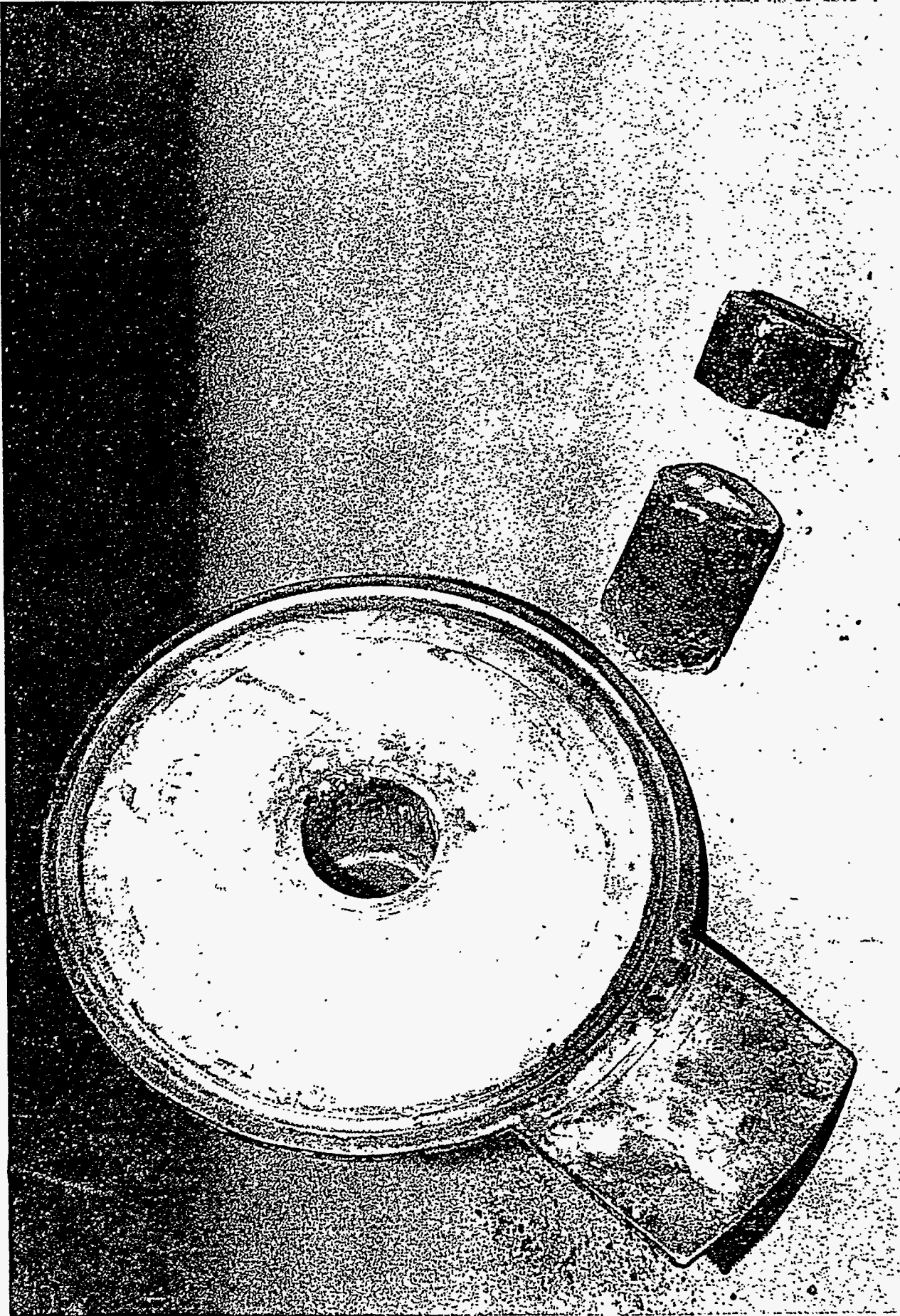


Figure 5.7. Copper crucible, processed vanadium ingot and slag "cap."

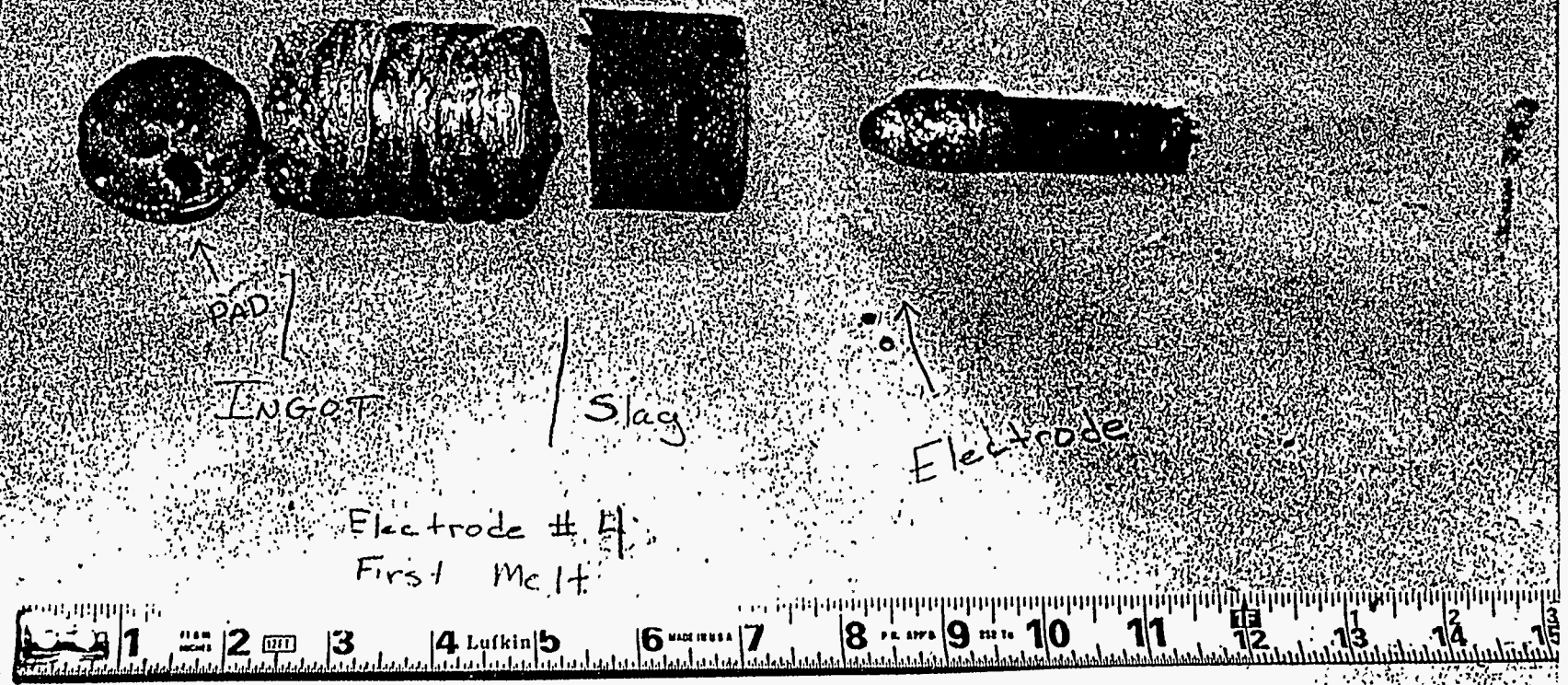


Figure 5.8. Arrangement of "pad", processed ingot, slag, and electrode position.



V-5Ti-5Cr Alloy
Electroslag Remelted in Vacuum
Cath Slag - 1500 amps - 80 V/Hz
Electrode # 5

Figure 5.9. As-processed vanadium electrode #5 (vacuum environment).

alloy electrode and the pad material at the bottom of the crucible. The electrode was quickly withdrawn to allow the slag to become molten. A good slag pool, i.e., one that completely covered the underlying vanadium starting material, was developed before the electrode was fed into the pool. As the electrode is fed into the pool drops of vanadium alloy melt off of the end and drop through the slag. Reactions to remove impurities can occur both at the electrode surface and within the slag pool. An ingot of the vanadium alloy reforms on the bottom of the crucible due to the cooling action of the water cooled copper crucible. When most of the electrode is melted the power is turned off and the furnace allowed to cool. Once cool, the copper crucible is removed and the vanadium alloy ingot and slag material is extracted from the crucible. Figure 5.7 shows a photograph of the copper crucible, the processed vanadium alloy ingot, and the slag "cap" extracted from the copper crucible. The crucible shown in Figure 5.7 has a 5.1 cm (2.0 in.) inner bore and is approximately 15.2 cm (6 in.) deep. Figure 5.8 shows the arrangement of the pad material, processed vanadium ingot, slag, and electrode stub.

All of the helium back-pressure tests resulted in runs having some duration of good continuous melting. The test in vacuum was more sporadic. The arc between the vanadium alloy electrode and the ground, i.e., the alloy melt, was unstable and much of the slag was splattered out of the crucible and onto the cold walls of the chamber. Melted alloy was also splattered onto the walls once the pool of slag was gone. Figure 5.9 shows the as-processed vanadium alloy ingot melted in the vacuum environment. The large pores are spaces left by slag inclusions.

5.3 Chemical Analyses

Chemical analyses for the as-processed ingots are shown in Table 5.3. Each ingot was cut in half, following processing, and chemical analyses samples extracted near the top and near the bottom of the ingot. Analyses were not completed for Electrodes 2, 3 and 5 because these runs did not show good stability during the process. Electrodes 2 and 3 were the first melts attempted and were used for setting voltage and amperage settings. Electrode 5 was run in a vacuum which resulted in unstable melting, arcing, and splattering as discussed above. Electrodes 1 and 4 produced runs that were more characteristic of good electroslag remelt operations. The more complete chemical analyses for these ingots showed some interesting trends. About forty percent of the manganese was removed from the electrode material. This was not predicted based upon the range of solubility of manganese in vanadium at most compositions as illustrated in the phase diagram for Mn-V in Figure 5.10, and also, the calculations shown in Table 3.4. Perhaps some manganese segregation results by electrorefining processes associated with reactions at the electrode, or migration of ionized species due to polarization conditions existing across the slag pool. Most of the yttrium and calcium was removed in the first run for both Electrode 1 and 4. Small amounts of each impurity were removed in a second melt of the ingots, but not enough to justify a second remelt to achieve higher removal efficiencies. Table 5.4 shows the average removal efficiencies obtained in Electrodes 1 and 4.

Table 5.3. Chemical analyses results from the electroslag remelted ingots¹.

Electrode 1 Analysis						
Ca (wt %)	Cr (wt %)	Mn (wt %)	Y (wt %)	Ti (wt %)	O2 (wt %)	Ar (ppb)
1FCa(T) -- First Melt (Top of Ingot)						
0.0161	4.77	0.201	0.0011	2.85	0.23	26
1FCa(B) -- First Melt (Bottom of Ingot)						
0.0147	4.65	0.200	0.0010	5.19	0.22	27
1SCa(T) -- Second Melt (Top of Ingot)						
0.0204	4.78	0.208	0.0002	3.03	0.28	13.5
1SCa(B) -- Second Melt (Bottom of Ingot)						
0.0147	4.65	0.200	0.0010	5.19	0.22	15
Average Removal Fraction ²						
0.95	0.0021	0.41	0.996	0.14	(-0.25)	0.995
0.94	0.0034	0.40	0.998	0.13	(-0.39)	0.998
Electrode 4 Analysis						
Ca (wt %)	Cr (wt %)	Mn (wt %)	Y (wt %)	Ti (wt %)	O2 (wt %)	Ar (ppb)
4FCa(T) -- First Melt (Top of Ingot)						
0.0182	4.67	0.200	0.0012	3.01	0.25	26
4FCa(B) -- First Melt (Bottom of Ingot)						
0.0140	4.06	0.192	0.0007	2.77	0.25	27
4SCa(T) -- Second Melt (Top of Ingot)						
0.0174	4.06	0.215	0.0002	2.79	0.23	14.5
4SCa(B) -- Second Melt (Bottom of Ingot)						
0.0181	4.36	0.191	0.0003	2.28	0.18	15
Average Removal Fraction ²						
0.94	0.071	0.42	0.997	0.39	(-0.39)	0.990
0.93	0.104	0.40	0.999	0.47	(-0.14)	0.995

¹ Removal fractions are based upon the input mixture composition reported in Table 5.1.

² (+) - Increase / (-) - Decrease in concentration

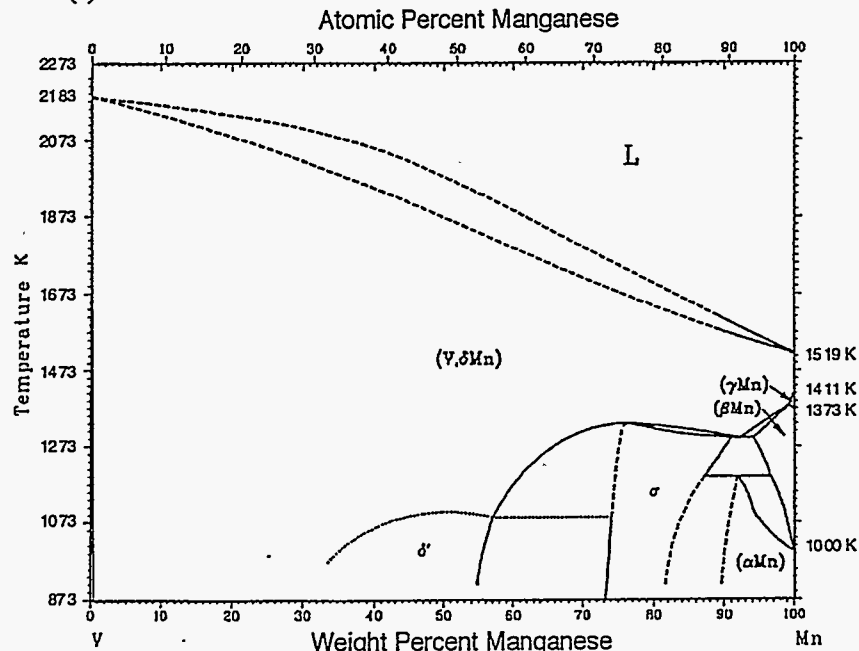


Figure 5.10. Mn-V phase diagram (Massalski, 1990).

Table 5.4. Summary of removal efficiencies.

	Calcium	Yttrium	Manganese	Argon
First melt	94	99.6	42	99.3
Second melt	93	99.8	40	99.7

Table 5.5 shows the results of the chemical analysis completed on the as-processed slag. It is important to note that slag material was removed between the first and second melts. The large difference between the amounts of Y found in the slag and the first melt and the second melt is due to the loss of this element to the first slag. The slag analyses indicate large retentions of yttrium with smaller retentions of manganese and chromium. Titanium and vanadium were the most abundantly found alloying elements in the slag. The amount of vanadium found in the slag, however, represented only 0.06 wt % of that in the ingot. This low loss of vanadium is favorable from a recycling standpoint. The titanium content in the slag translates into 0.12 wt % of that in the ingot, i.e., 2.5 percent of the titanium initially present. Data in Table 5.3 show that substantially more (from 15 to 50 wt %) was lost from the remelted ingots. This shows that much of the titanium evaporated from the slag and deposited onto the walls of the furnace. This was observed as very reactive fine powder when the furnace was disassembled following the runs. Titanium loss has been a problem which has been resolved in processing some of the precipitation hardened nickel base alloys. Perhaps changing the chamber gas, gas pressure, melt rate, or etc. could reduce the amount of titanium lost from the alloy. We observed that greater amounts of titanium, and also chromium, were lost from Electrode 4 than from Electrode 1 (shown in Table 5.3). This indicates that some unknown parameter was different between the two tests and suggests that the process can likely be optimized to decrease titanium loss.

Table 5.5. Results of chemical analyses from slags for electrodes 1 and 4.

Slag from Electrode 1				
Cr (wt %)	Mn (wt %)	Y(wt %)	Ti (wt %)	V (wt %)
1FMS - - First Melt				
0.0310	0.0145	0.5450	0.35	0.03
1SMS - - Second Melt				
0.0434	0.0214	0.0058	0.60	0.29
Slag from Electrode 4				
Cr (wt %)	Mn (wt %)	Y(wt %)	Ti (wt %)	V (wt %)
4FMS - - First Melt				
0.0268	0.0130	0.5440	0.16	0.03
4SMS - - Second Melt				
0.0245	0.0147	0.0018	0.45	0.11

5.4 Metallurgical Observations

Metallurgical examinations were performed at the Idaho National Engineering Laboratory on the remelted ingot from Electrode 4. The ingot was sectioned through the center, ground, and etched with hydrofluoric acid. Figure 5.11 is an SEM micrograph of the as-processed ingot at a magnification of 20. The fine columnar dendritic microstructure is generally dependent upon the alloying agents present and the cooling rates experienced during processing. Standardless EDS microprobe analyses were performed at four locations on this sample. Table 5.6 shows the results from these analyses. The EDS analyses show that the remelted ingot is very homogeneous. Homogeneous material is usually found in alloys processed by electroslag remelting. It is important to note that these values represent the vanadium alloy following processing. The levels of the titanium and chromium are close to, but slightly lower than the input concentrations. This agrees with the loss of these elements from the alloy shown in Table 5.3 and the gain of the elements in the slag shown in Table 5.5. Manganese was not detected with the standardless EDS analyses. The manganese peak was likely masked by another element in the spectra since chemical analyses have shown that it was present. Iron seen in the EDS analyses at levels near those observed in the original electrodes supports the idea that the iron stems from contamination in the original powder mixture.

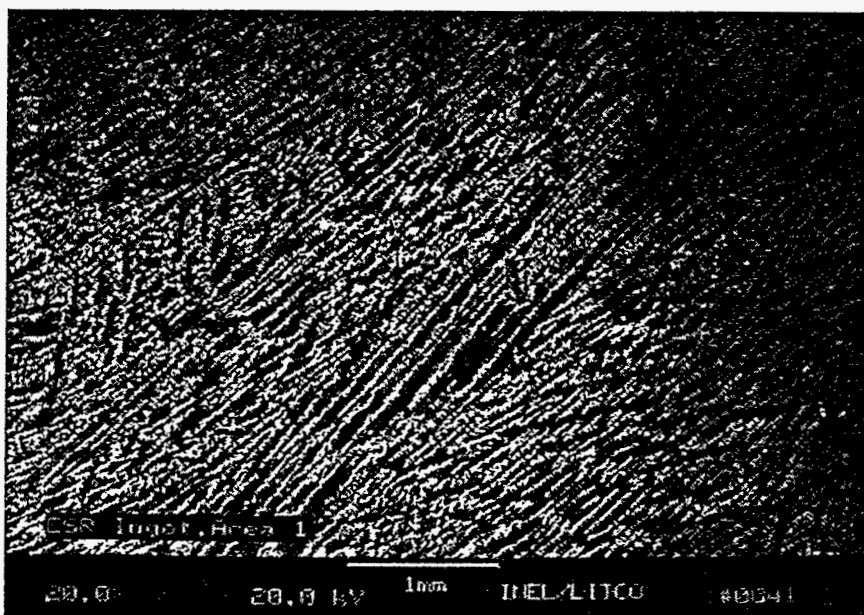


Figure 5.11. As-cast microstructure of electroslag remelted vanadium electrode 4.

Photographs of the sectioned ingot resulting from the first and second melts of Electrodes 1 and 4 are shown in Figures 5.12 and 5.13, respectively. These photographs show that there were some slag inclusions in the upper and lower regions of the as-processed ingot. There are also some voids in the ingot that appear to be the result of gas pockets. Gas pockets have sometimes been associated with procedures used in slag preparation, or they

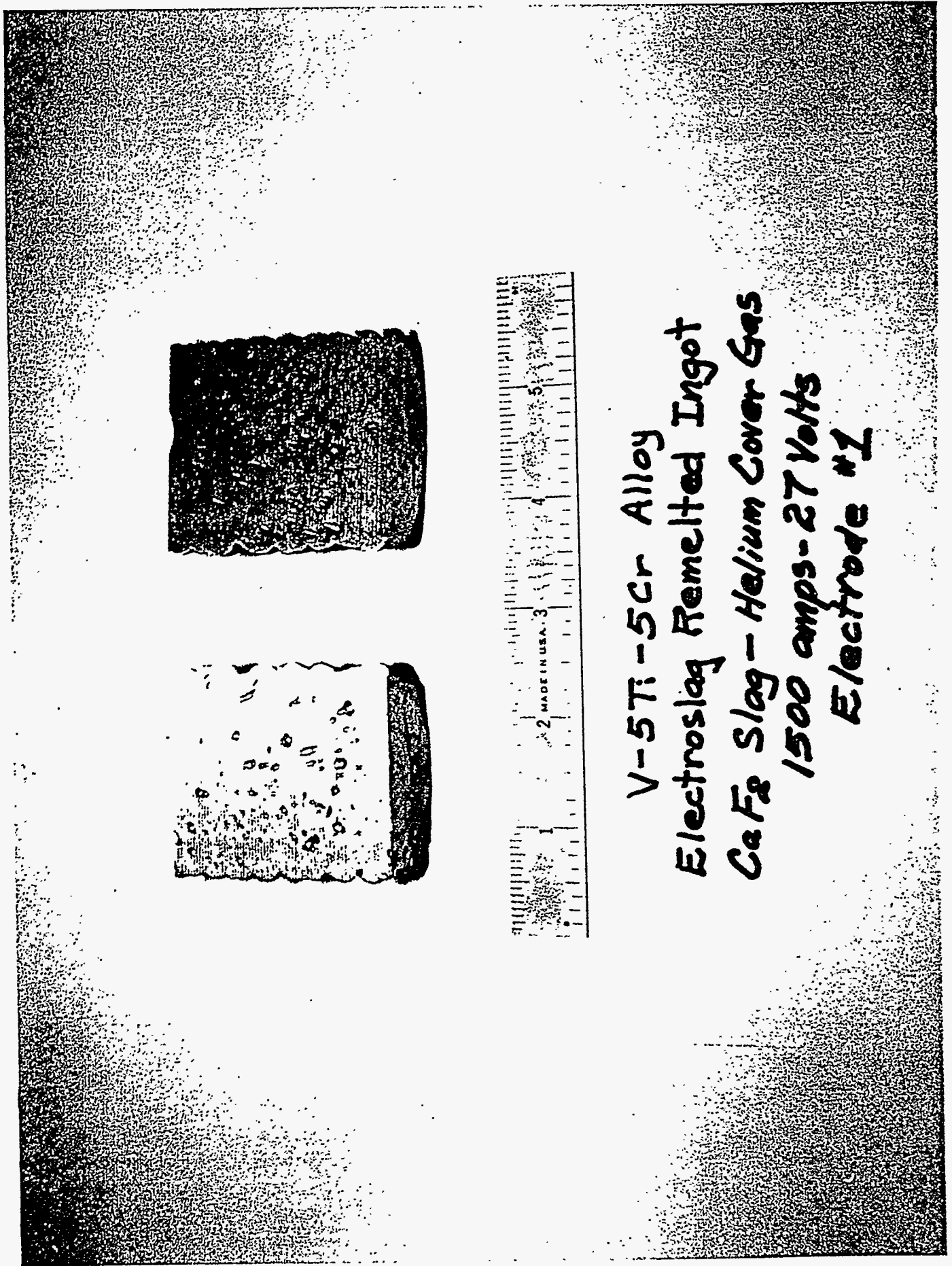


Figure 5.12. Sectioned ingot from first melt of electrode 1.

Table 5.6. Standardless EDS microprobe analysis results.

Analysis #	V (wt %)	Ti (wt %)	Cr (wt %)	Mn (wt %)	Fe (wt %)
1	91.38	4.22	4.27	0.0	0.13
2	91.45	4.05	4.21	0.0	0.29
3	91.15	4.20	4.41	0.0	0.24
4	91.24	4.28	4.36	0.0	0.12
Average	91.31	4.18	4.31	0.0	0.20

could possibly result from some contamination in the fabricated electrodes. The presence of such defects do not reflect the maximum capabilities of the electroslag remelting process for vanadium alloys. The purpose of the current investigation was to demonstrate removal efficiencies of certain impurities. Optimizing process parameters and ingot quality was not within the scope of this study. The availability of material limited the size and number of the fabricated electrodes. This resulted in ingots having significant portions from the start-up and shut-down phases and a limited amount from steady state melting. Ideally, the laboratory scale remelted ingots should be a minimum of 20 to 25 cm (8 to 10 in.) in length to allow stable conditions in the arc, slag pool, melting, and chemical and electrochemical processes to be attained. The quality of electroslag remelted ingots have been shown in previous titanium research to improve with scale-up. The size of operation that might be involved for recycling operations for a fusion reactor could produce ingots 15 to 60 cm in diameter and several meters long. This would likely improve the quality of material within the bulk of the ingot and increase the ratio of the ingot undergoing steady state melting compared to the end regions.



Figure 5.13. Sectioned ingot from second melt of electrode 4.

6.0 SUMMARY AND CONCLUSIONS

A scoping investigation to determine the feasibility of using electroslag remelting to remove intentionally added impurities, as surrogates for activated isotopes, from a V-5Ti-5Cr alloy was completed. Non-radioactive isotopes of these elements were added by powder metallurgy method to an alloy system about equivalent to V-5Ti-5Cr (yttrium was substituted for scandium). The changes in the concentrations of these elements in electroslag remelted ingots were then determined. The electroslag remelting operations were accomplished using a laboratory scale furnace with pure CaF_2 as a flux and helium as a cover gas.

The study has shown that the relatively reactive, high melting point vanadium alloy can be electroslag remelted. The amount of vanadium lost during the remelt process was minor (0.06 wt %) and oxygen increased from about 0.18 wt % to about 0.25 wt %. Yttrium and calcium were nearly completely removed from the remelted material, 99 and 93 percent, respectively. About forty percent of the manganese was removed. Argon analysis indicates that greater than ninety-nine percent of the gas was removed during processing. Significant amounts of the two major alloying elements, up to 50 wt % of the titanium and up to 10 wt % of the chromium, were lost during the process. Slag analyses showed that these elements were also evaporated from the slag. Future process refinements would be needed to reduce such losses to maintain alloy chemistry and limit activated product dispersion by evaporation.

The removal of some of the impurities appeared to be accomplished by electrochemical processes active within the polarizing conditions in the slag pool. Chemical thermodynamic equilibrium calculations involving the molten alloy and slag systems are not effective in predicting the removal of some impurities such as manganese. Additional research would be needed to understand the mechanisms involved in the refining processes. However, this study has shown that some critical isotopes can be removed from future irradiated vanadium by electroslag remelting. The method from other applications has shown a suitability for scale-up to handle large tonnage melts. This process could therefore be a viable method to reduce the lead time for recycling the material back into service in a fusion reactor.

ACKNOWLEDGEMENT

This work was performed under the auspices of the U.S. Department of Energy, contract DE-AC07-94ID13223, and was supported by the Office of Fusion Safety and the Laboratory Directed Research and Development Program.

Special acknowledgment is extended for the electroslag remelt experimental work completed at the Bureau of Mines, Albany, Oregon by Ralph H. Nafziger and Ed Argetsinger. Mick Kunk performed the argon analysis by the Ar^{39}/Ar^{40} analysis technique at the U.S. Geological Survey, Reston, VA.

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