

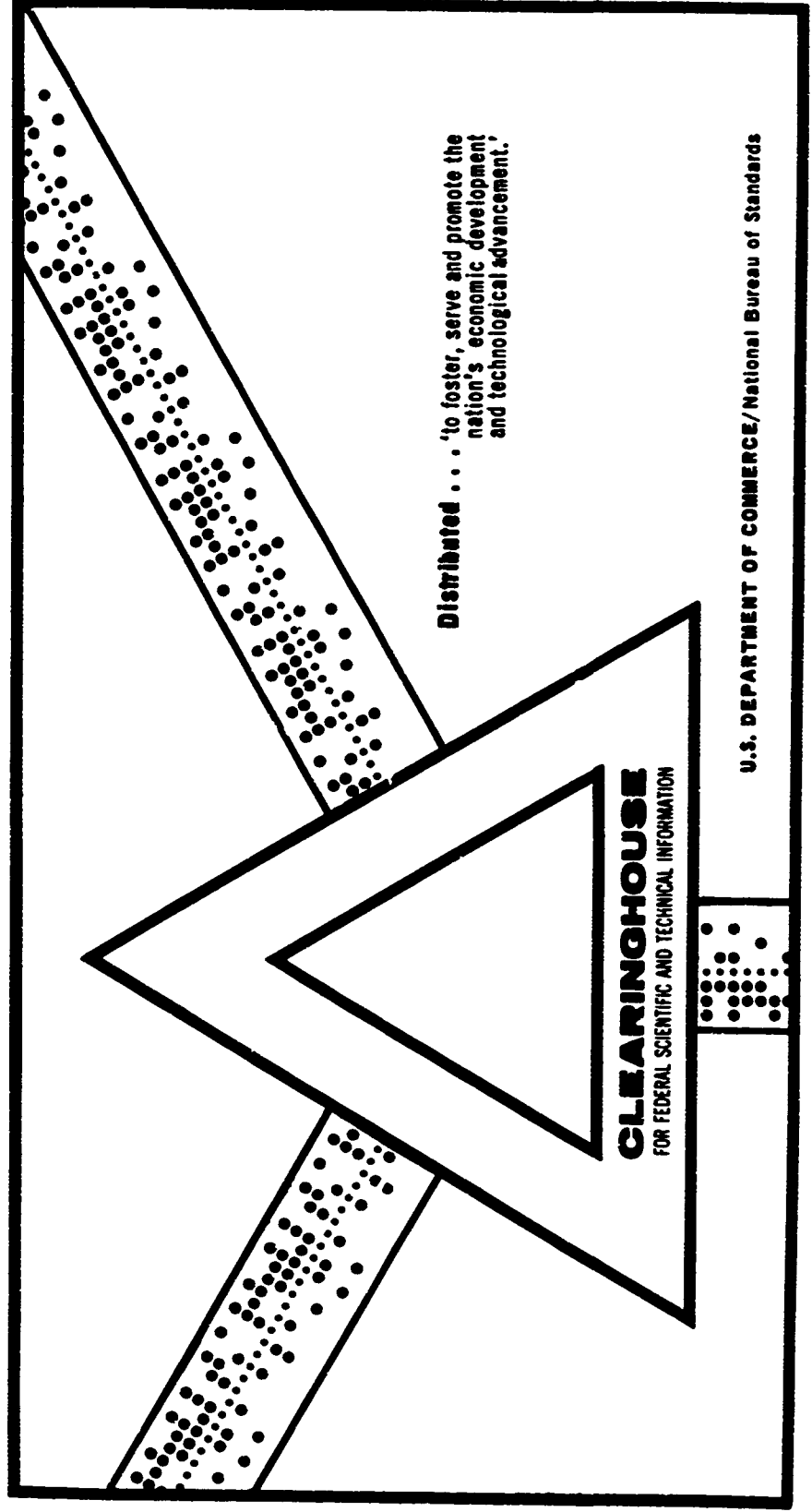
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TITANIUM MELTING BY THE ELECTROSLAG PROCESS

R. A. Beall, et al

Bureau of Mines
Albany, Oregon

19 November 1969



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TOPICAL REPORT

to

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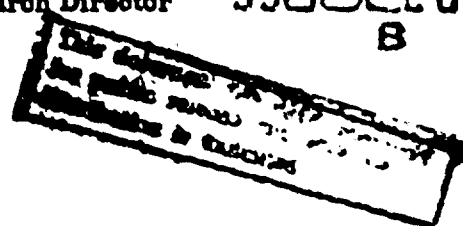
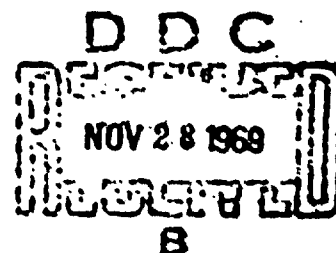
Contract MIPR No. AW-7-1

TITANIUM MELTING BY THE ELECTROSLAG PROCESS

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**Albany Metallurgy Research Center
Albany, Oregon
H. Gordon Poole, Research Director**





UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

P. O. BOX 70
ALBANY, OREGON 97321

November 19, 1969

Mr. S. V. Arnold
U.S. Army Materials and
Mechanics Research Center
Watertown, Massachusetts 02172

Dear Mr. Arnold:

This report is the final summary of the work on the project "Slab-Shaped Titanium Ingots by Cold-Mold Arc Melting," MIPR No. AW-7-1. This work was sponsored by the Army Materials and Mechanics Research Center beginning in June 1965 and terminating in September 1968. The research was conducted in the Metals Processing Projects group at the Albany Metallurgy Research Center.

Yours truly,

A handwritten signature in dark ink, reading "H. Gordon Poole", is written over the typed name.

H. Gordon Poole
Research Director
Albany Metallurgy Research Center

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TOPICAL REPORT

TITANIUM MELTING BY THE ELECTROSLAG PROCESS

by

R. A. Beall, P. G. Clites, R. H. Nafziger, and J. T. Dunham

Manuscript completed September 1968. This report covering the development of methods of production of slab-shaped titanium ingots by cold-mold electroslag melting, under Contract MIPR No. AW-7-1, is transmitted to you directly from this laboratory of the Bureau without prior review by the Office of the Director. Republication in any form, except for official use as originally agreed, is contingent upon approval of the Director.

**BUREAU OF MINES
ALBANY METALLURGY RESEARCH CENTER
ALBANY, OREGON**

TITANIUM MELTING BY THE ELECTROSLAG PROCESS

by

R. A. Beall ^{1/}, P. G. Clites ^{2/}, R. H. Nafziger ^{3/}, and J. T. Dunham ^{4/}

ABSTRACT

This report deals with the melting of titanium by the electroslag or Hopkins process. Details are given on the slag chemistry. Both small and large scale melting experiences are covered. Ingot quality is described in terms of chemistry and workability. Primary problems remaining are hydrogen removal and effect of residual fluorides.

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INTRODUCTION

This is a final report covering the activities at the Albany Metallurgy Research Center on the program to develop a technique for production of slab-shaped titanium ingots. An essential point of the program is the use of the electroslag or Hopkins Process to achieve the objective. This report covers the period September 1966 to July 1968. An earlier report (3) ^{5/}covers details of the first year of the program; several publications (2, 4, 1) have resulted from the work.

In brief, titanium is conventionally double melted in a consumable electrode arc furnace in vacuum, and in a water-cooled crucible. These unusual features are necessitated by the reactivity of titanium to atmospheric gases and to conventional crucible materials.

The Hopkins Process utilizes a resistive slag as a heat source rather than an arc, but the consumable electrode and the water-cooled crucible are similar if not identical in both processes. Figure 1 shows a comparison of the two.

The electroslag process has recently gained considerable attention in the United States as a technique for steel melting. Recent disclosures in the USSR (8, 9) led to interest in the electroslag process for titanium. The Russian

^{5/} Underlined numbers in parentheses refer to items in the references at the end of this report.

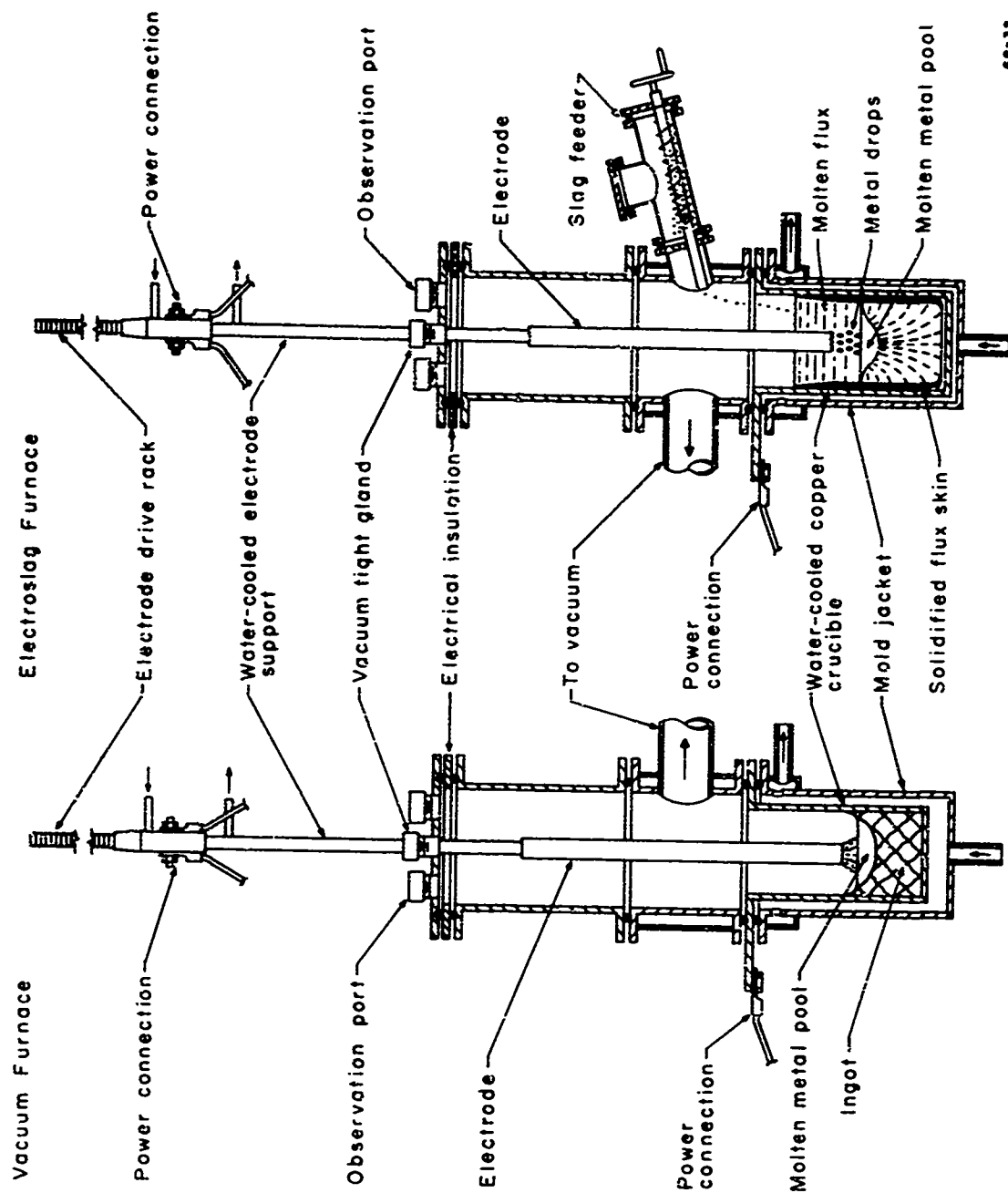


FIGURE 1. - Comparison of Arc and Electroslag Melting

literature showed that the process was being heavily utilized for steel making in slab shapes and was the subject of research for titanium. To confirm the Russian claims on titanium and to develop know-how in the United States, a cooperative program was instituted between the Army and the Bureau of Mines in July 1965. Some of the benefits initially expected from the electroslag technique were: (1) improved directionality of cooling, (2) controlled and slower melt rate, (3) shallow pool, (4) reduction in segregation, (5) improved sidewall, (6) reduction in loss of volatile components, (7) the possibility of single melting by electroslag as a substitute for the present commercial practice of double (or triple) melting the sponge, and (8) slab-shaped ingots. Now that the research has proceeded for three years, the list of potential benefits has been modified somewhat.

Practically all of the titanium ingot produced in the United States by the vacuum-arc process is cylindrical in form. However, from a forging and rolling standpoint, rectangular cross sections would lead to more efficient operations. Bureau research and development in 1956 (15) showed that arc-melted ingots could be prepared in slab shapes with three-phase ac power. The inconvenience of the mechanical designs prompted by the three-phase ac, however, discouraged industrial exploitation of the work.

The USSR reports indicated that slab shapes were feasible and practical with the electroslag process. Hence, this aspect of the process was included as an important facet of the work reported here.

TITANIUM SPONGE

It was a primary thesis of this development effort that a single electroslag melt of titanium sponge could replace the conventional double-vacuum arc melt to prepare forgeable titanium ingots. Gurevich (8) based his work on the same thesis.

Titanium sponge, however, is not a uniform material as far as the products of the several sources are concerned, and a melting process suitable for one type is not necessarily suitable for all types of sponge. For instance, one firm utilizes a magnesium reduction of TiCl_4 to form sponge which is subsequently leached with an aqueous solution and then dried. Another firm reduces the tetrachloride in two steps with sodium, and leaches the resultant sponge. A third producer depends on a magnesium reduction followed by, either a gas-sweep system, or water leach, or both. Imported sponge is usually magnesium-reduced, and purified in vacuum to remove excess magnesium and chlorides. Electrolytic titanium which may be used in place of sponge, is now available on the market for a premium price.

Each process variation leads to product variation. Sodium-reduced sponge tends to have finer particle sizes than does magnesium-reduced sponge. Magnesium chloride is more likely to be trapped or occluded in magnesium-reduced sponge. Water-leached magnesium-reduced sponge can be expected to have a higher hydrogen content than water-leached sodium-reduced sponge. Vacuum-distilled sponge should be lower in both chloride and hydrogen than leached sponge.

The relation of the above properties to melting technique is this: the electroslag process, as presently practiced at the Bureau, does not give the same opportunity for removal of hydrogen, excess reductant and volatile salts as does the vacuum-arc process. Therefore, in the discussions below, it is important to note the sponge source, since this is a significant factor.

SMALL-SCALE RESEARCH

General

"Small-scale research" is defined for the purpose of this report as work conducted in a furnace fitted with a 4-inch-diameter crucible or a 3-inch by 7-inch slab-shaped crucible. Ingots of titanium prepared in this furnace weigh about 15 pounds for round ingots and 25 pounds for slab-shaped ingots.

The main objective of this portion of the work was to establish information that would contribute to the melting of larger ingots, particularly in the prototype production furnace.

The first work undertaken was (1) to establish melting conditions so that quality ingots could be obtained consistently and (2) to characterize the ingot quality by an evaluation of impurity content, fabricability, and mechanical properties determined on products wrought from the ingots. As discrete ingot characteristics related to melting practice were anticipated, replicate ingots were prepared by double vacuum arc melting sponge from the same source as used for electroslag melting, and the necessary data determined so that a direct comparison could be made between materials representing the two methods of melting.

The work was then extended to include two titanium alloys. One contained 6-percent aluminum and 4-percent vanadium. This alloy was selected for study because of its popularity for industrial application. The other alloy contained 8-percent manganese and was selected for study because it is difficult to prepare by conventional vacuum arc melting techniques without segregation.

In an adjunct study, experiments were conducted to establish the effects of alternate power sources for electroslag melting and to determine if the slag cover afforded adequate protection of the titanium during melting to eliminate, or at least reduce, the requirement for an inert furnace atmosphere. Alternate power sources included alternating current and reverse-polarity direct current; straight-polarity (electrode negative) direct current for melting is considered conventional in our laboratories. Alternate furnace atmospheres studied were either air or helium flowing under a positive pressure as opposed to the conventional closed furnace containing helium at reduced pressure. Combinations of the different power sources and furnace atmospheres were included in the study.

One experimental ingot was made by electroslag melting an electrode pressed from alloy scrap turnings, and one ingot of a columbium alloy was electroslag melted. An attempt was made to melt by the "b-filar" technique

Equipment

The main equipment for the work was the melting furnace with the associated vacuum system and power supplies. The same basic furnace components were used for both electroslog melting and vacuum-arc melting. The water-cooled copper crucible for electroslog melting was either cylindrical with an inside diameter of four inches, or a tapered slab-shaped crucible approximately 3-inches by 7-inches in cross section with corners 1-1/2-inches in radius. The crucibles were cooled during melting with water flowing at about 50 gallons per minute under 30 psi pressure. The slag feeder, attached to the furnace chamber, was operated manually by cranking the auger. (Details of furnace construction may be found in the first year's report (3).)

For both electroslog melting and vacuum arc melting the electrode was fed into the crucible by manually energizing a small brake-motor drive unit. The rate of electrode feed was regulated by monitoring the ampere and volt meters.

The vacuum system for evacuating the furnace was a conventional mechanical pump having a free air capacity of 50 liters per minute. Adequate evacuation was considered to be met when 50 microns of pressure was achieved with a maximum leak rate of 5 microns per minute. Generally, the leak rate was less. For vacuum arc melting a dynamic vacuum was maintained throughout melting. For electroslog melting the furnace was evacuated, isolated from the pump, and backfilled to a partial pressure of helium, usually to one-third atmosphere.

When melting with direct-current power, the furnace was connected to the main power supply of the melting laboratory. This power supply consisted of a parallel bank of air-cooled welding rectifiers (selenium) of 1,000 amperes capacity each. The total capacity of the bank was over 15,000 amperes at 35 volts. The open circuit potential was 70 volts. Power control was by saturable reactor for the individual rectifiers. As a group, the power was controlled by switching the units in or out of the circuit. The furnace could be connected to the power supply for either straight-polarity (electrode negative) or reversed-polarity melting.

The alternating-current power supply consisted of three welding transformers connected in parallel. Rated capacity of each transformer was 1,500 amperes at 45 volts. Open circuit potential was 90 volts. Power control was by manually-controlled motor-driven movable cores in the transformers.

Other equipment included a hydraulic press for briquetting sponge into compacts and a vacuum welding tank for welding the compacts into electrodes. All welding on titanium was done in the tank with a nonconsumable thoriated tungsten electrode.

Materials

The sponge electrodes were prepared for melting by briquetting 10-inch-long rectangular bars, generally 2-inches by 2-inches in cross section, and butt welding the bars together. The density of the briquetted bars was 0.14 pounds

per cubic inch. The bars or electrodes were stored in a drying oven at 150° F until charged into the melting furnace. Electrode materials for preparing alloy ingots are described in that section of the report.

The slag used for all melts in this portion of the work was treated reagent-grade calcium fluoride. The treatment and purity of the slag will be discussed.

Electroslag Melting Versus Vacuum Arc Remelting

To obtain a realistic evaluation of ingots made by electroslag melting titanium sponge, electroslag-melted ingots were compared directly with double vacuum arc melted ingots prepared from the same sponge source and in the same melting furnace. This minimized differences arising from variation in sponge lots and from melting practice.

Procedures

Vacuum Arc Melting:

The furnace was charged with the electrode and with 200 to 300 grams of loose sponge as a starting base. The furnace was evacuated to the required pressure and the arc started with 1,000 to 1,500 amperes at about 30 volts, straight-polarity direct current. Once a molten pool of metal was formed, the power was raised to 3,500 to 3,800 amperes at 30 volts. At the end of the melt the power was reduced to hot-top the ingot.

First-melted ingots were machined to remove the porous surface, spatter collar, and unmelted sponge particles from the ingot bottom. The machined ingot was quartered, sampled if necessary, rewelded into an electrode and remelted with the same procedure.

Electroslag Melting:

Procedures for electroslag melting were based on the experience and data reported earlier (3). The furnace was charged with base material and electrode similar to arc melting, evacuated, and then backfilled with helium to one-third atmosphere of pressure. An arc was started and a pool formed with the same current and voltage used for arc melting. Slag was then rapidly introduced into the crucible and the power level raised, as the mode changed from arc to electroslag.

At first it was necessary to vary the power input and the depth of slag cover to determine optimum conditions for obtaining good ingot sidewalls. Good sidewalls were highly desirable so that the ingots could be converted to rolled plate and sheet without prior surface conditioning.

Melts were made with slag depths varying from 1-1/2 to 2 inches deep and with currents of 4,500 to 4,800 amperes and a potential of 20 to 23 volts. Ingot surfaces were excellent. For this size ingot, 4-inches in diameter, best ingot sidewall surfaces were obtained with the slag cover depth between 1-1/2 and 2 inches, a current of 4,500 amperes, and a potential of 20 to 22 volts.

For slab-shaped ingots, 3-inches by 7-inches in cross section, smoothest ingot surfaces were obtained with a slag cover of 2 to 3-inches deep, a melting current of 4,500 amperes and a potential of 30 volts. Electrodes for melting into slab-shaped ingots were 4-inches wide and 1-1/2-inches thick.

Slab-shaped ingots melted under the optimum conditions appeared equivalent to round ingots in surface quality. Because round ingots were easier to prepare, they were used for most of the small-scale work.

Comparison of Vacuum-Arc-Remelted and Electroslag-Melted Ingots

Melting:

Ingots prepared by vacuum-arc melting were melted twice. Ingots prepared by electroslag melting were melted only once. The typical data collected below show electrical conditions and melting efficiencies for the two methods with straight-polarity direct-current power:

<u>Method</u>	<u>Current, amps.</u>	<u>Potential volts</u>	<u>Melting rate, lbs/ min.</u>	<u>Power utilization, kw-hr/ lb</u>
Vacuum arc	3,800	30	3	0.6
Electroslag	4,500	22	2	0.8

The higher melting rate and lower power utilization show vacuum arc melting the most efficient; however, it was necessary to vacuum arc melt twice to obtain sound ingots. It was also shown that hot-topping was much more efficient with electroslag melting than with vacuum arc melting. Shrinkage pipes were easily eliminated when electroslag melting. At the end of a vacuum arc melt,

hot-topping reduced the size of the shrinkage cavities, but did not eliminate them completely.

Ingot Quality:

Sidewalls of the electroslag-melted ingots appeared superior to those of vacuum-arc-remelted ingots, mainly because of freedom from sub-surface porosity. Electroslag-melted and arc-melted ingots were sound. Structures of ingots prepared by the two melting methods were compared in the earlier report (3). Although ingot structure, including grain size and grain orientation generally influences fabricability, no differences were noted in hot working the small titanium ingots prepared by either method. This may not be true for alloy ingots, but no such studies have been made in this laboratory. Fabrication of unalloyed titanium ingots is discussed later.

Typical analyses for ingots prepared by the two melting methods are shown in table 1. The only significant difference is the fluorine content. No evidence of fluorine could be found in samples from vacuum-arc melted materials; however, it was always present in samples from the material prepared by electroslag melting. Additional ingot fluorine analyses are included in table 15. The uncertainty of these data is ± 50 percent.

No definitive conclusions can be reached concerning fluorine content as a function of slag composition or prior slag treatment. Other parameters being equal, the fluorine potential in a more stable fluoride slag is lower and is less likely to contribute fluorine to the metal.

TABLE 1. - Typical analyses ^{1/}for ingots prepared by vacuum arc remelting and electroslag melting.
All values in parts per million

Melt number	Type of Melt	Location ^{2/}	O		H		F	C	N	Al	Cu	Fe	Mg	Si	Sn
			Edge	Center	Edge	Center									
SA 26, 109	Vacuum arc remelt	Top	856	807	14	17		73	51	<50	<50	300	<15	100	<180
		Bottom	633	717	16	17		77	48	<50	<50	400	<15	200	<180
SA 25, 897	Electroslag melt	Top	748	752	18	17	90	86	66	<50	400	400	80	200	<180
		Bottom	1150	836	17	12	80	183	78	100	200	400	80	250	<180
SA 26, 046	Vacuum arc First melt	Top	819	787	18	19		33	119	<50	100	1000	<15	100	<180
		Bottom	618	976	19	16		31	94	50	<50	500	15	200	<180
SA 26, 061	Electroslag melt of SA 26, 046	Top	949	838	27	19	109	67	<50	100	400	400	15	200	<180
		Bottom	1012	804	21	25	161	72	50	300	400	400	30	300	<180

^{1/} Oxygen by inert gas fusion;
Hydrogen by hot extraction;
Nitrogen by Kjeldahl method;
Fluorine by a sensitive electrode method;
Carbon by combustion.

All others by optical emission spectroscopy.

NOTE: Ca, Cr, Mn, Mo, Ni, and V all less than 50 ppm.

^{2/} Top location: From 1 to 2 inches below top of ingot.
Bottom location: From 1 to 2 inches from bottom of ingot.

TABLE 2. - Impurity contents of titanium specimens for corrosion testing

Material	Impurity							
	Al	C	Cu	F	Fe	Mg	N	Si
SA 25, 904, sheet, reduced 50 pct in thickness by cold rolling. Electroslag-melted								
Ti - - - - -	50	79	<50	175	300	50	60	150
								<180
SA 26, 110, sheet, reduced 50 pct in thickness by cold rolling. Vacuum arc re- melted Ti - - - - -	<50	115	<50	<50	300	<15	47	100
								200

All values in ppm.
Ca, Cr, Mn, Mo, and V contents on all material: <50 ppm.
Ni: <35 ppm on all material.
Pb: <200 ppm on all material.

Microprobe analyses for fluorine on swaged rods showed no fluoride grains present in vacuum-arc-melted material but well dispersed particles (1 to 5 microns) over the sample surface of electroslag-melted titanium. This may be TiF_3 , inasmuch as no calcium was detected. The above result is unexpected from a thermochemical standpoint (see table 10). The absence of calcium indicates that the slag was not physically entrapped in the metal. Similar fluoride grains were also noted in titanium which had been slag-melted in an air atmosphere.

In order to determine if the above mentioned fluorine impurity found in electroslag-melted titanium is detrimental to the corrosion resistance normally observed in vacuum-arc-melted material, coupons from cold-rolled sheet have been subjected to corrosion testing at the College Park Metallurgy Research Center. Impurity contents of the submitted material are shown in table 2. Testing media were "substitute" sea water, which normally does not corrode titanium, and dilute H_2SO_4 , which normally corrodes titanium very slowly. Results indicated that a residual fluorine content of 100 ppm did not reduce the corrosion resistance of these samples (see Appendix)

Chlorine contents in selected ingots melted under various $CaCl_2$ - CaF_2 slags were all less than 20 ppm

To determine what impurities, other than fluorine, would be added to the titanium during melting, a sponge electrode was vacuum-arc melted into an

ingot, the ingot quartered and sampled, and then remelted by the electroslag method. The final ingot was sampled so that impurities could be compared before and after electroslag melting. Results are shown (last two melt numbers SA 26, 046 and SA 26, 061) in table 1. No significant contamination is shown. Fluorine was not determined, but it can be assumed that some contamination occurred. The slight increase in carbon was attributed to the slag purification treatment.

The hydrogen content shown in table 1 for electroslag-melted ingots is quite acceptable, however, in earlier work where ingots were melted from water-leached sponge, which contains about 200 ppm of hydrogen, the hydrogen content was not lowered during electroslag melting (3).

Fabrication:

Ingots produced by electroslag melting were fabricated to plate, sheet, and rod without prior conditioning of the ingot sidewalls. Ingots formed by double vacuum arc melting were machined before forging. Shrinkage cavities were removed by cropping the tops from ingots prepared by vacuum arc melting. The electroslag-melted ingots were free of shrinkage defects, but contained unmelted sponge particles in the bottom. These were removed by cropping the bottoms. A uniform size of ingot for forging was maintained by cropping both ends from all ingots.

Fabrication procedures were the same for ingots from both melting processes. Ingots were heated for two hours at 900° C and then press forged to 2-inches thick by 4-inches wide in three workings with reheats between workings. The forgings were then reheated and rolled to 1-inch thickness. The slabs, after conditioning by sand blasting, were reheated to 900° C for 30 minutes and cross rolled to plate 1/2-inch thick by 8-inches long. Break-down forging to obtain rod was similar. Ingots were initially forged to bars 1-1/2-inches in cross section, then forged round.

Secondary working of plate and rod was accomplished by heating to 850° C for 30 minutes, working from one to three passes, and reheating 10 minutes to temperature. Reduction, in either the rolling mill or rotary swage, was approximately 10 percent per working pass. After working to the final dimensions, 1-inch-diameter for rods and 1/4-inch thick for plates, the material was alpha annealed at 700° C for one-half hour. Hot-rolled and cold-rolled sheet, 1/16-inch in thickness, was prepared from 1/4-inch-thick plate. Hot rolling was done between 800° and 850° C. Material for cold rolling was hot rolled to adjust thickness and then annealed at 700° C for one-half hour. Cold-rolling reductions, ranging from 10 to 50 percent, were made by taking 10-percent reductions each pass. Both materials were fabricated without difficulty. No difference in workability was apparent.

Tests and Results

Tensile Tests:

Tensile properties were obtained for swaged rod and rolled plate in the alpha-annealed condition, and for sheet in both the hot- and cold-rolled conditions. Specimens were prepared and tested according to the procedures recommended by the American Society for Testing and Materials. Specimens from rods were 1/2-inch-diameter rounds with a 2-inch gage length. Specimens from plate and sheet were 1/2-inch wide with a 2-inch gage length. The specimens were tested with a 60,000 pound Baldwin tensile-testing machine at a straining rate of 0.05-inch/inch/minute.

Results from room-temperature tests for rod and plate specimens are shown in table 3. Tensile fractures for the two materials, vacuum-arc remelted and electroslog-melted, were similar.

Transverse sheet tensile properties are compared in figures 2 and 3 for material prepared by the two melting processes. The zero percent cold-work data were for hot-rolled sheet; the rest of the data were obtained on sheet cold rolled from material in the alpha-annealed condition.

Longitudinal tensile properties were also obtained for the rolled sheet. Strength properties were slightly lower, and elongation values showed corresponding increases.

TABLE 3 . - Average $\frac{1}{2}$ tensile properties of plate and swaged rod in the alpha-annealed condition

Ingot	Orientation	Tensile strength, psi	Yield strength, 0.2% offset, psi	Elongation, pct. in 2 inches	Reduction in area, pct.
<u>ROD</u>					
Vacuum-arc remelted	Longitudinal	57,000	37,300	40	65
Electroslag-melted	Longitudinal	60,000	45,000	34	60
<u>PLATE</u>					
Vacuum-arc remelted	Longitudinal	57,000	41,300	35	68
	Transverse	57,400	47,300	33	63
Electroslag-melted	Longitudinal	55,200	40,600	37	66
	Transverse	54,500	43,400	37	67

$\frac{1}{2}$ Average of at least four tests.

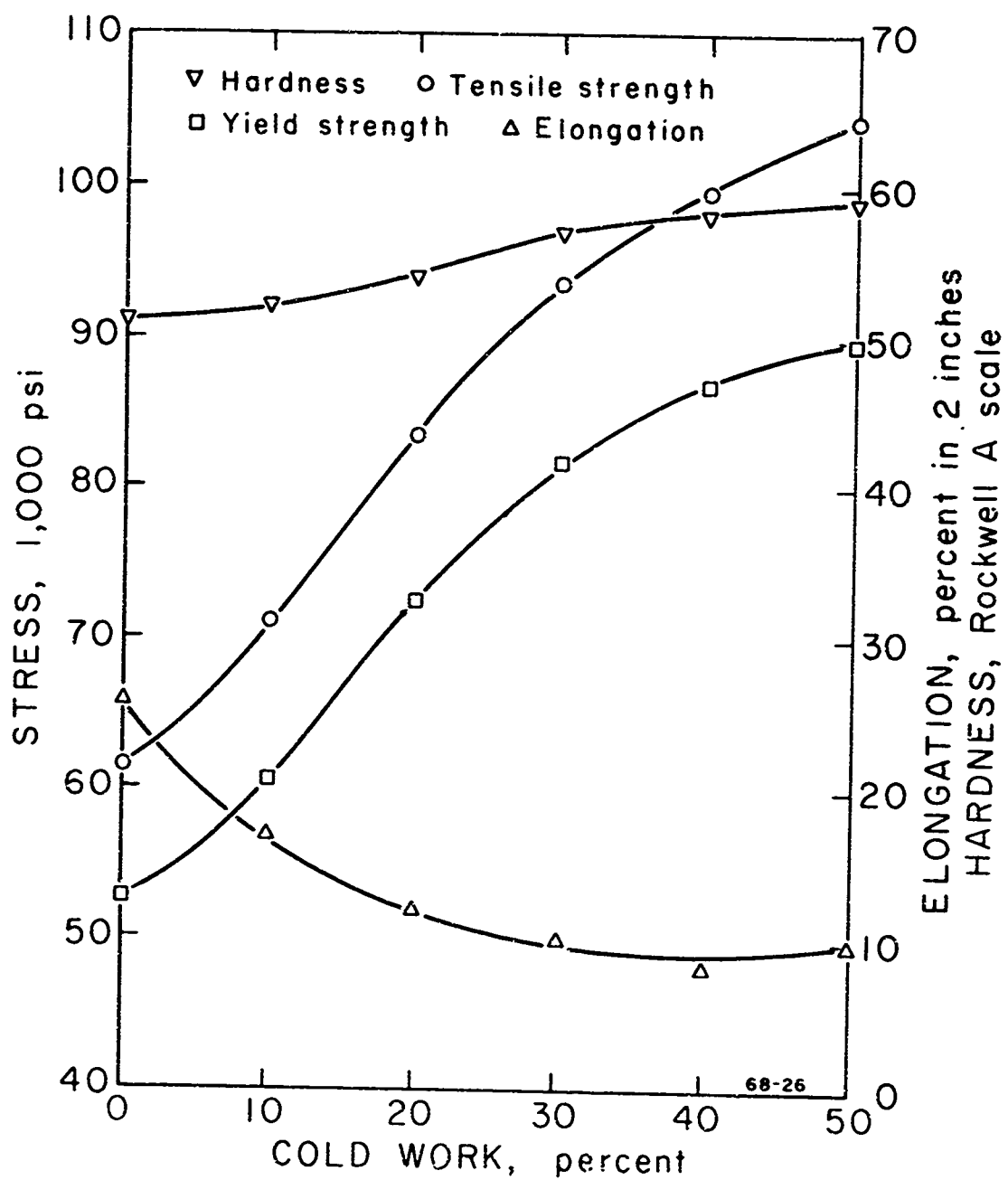


FIGURE 2. - Transverse Tensile Properties and Hardness of 1/16-inch-thick Sheet, Vacuum-Arc Remelted

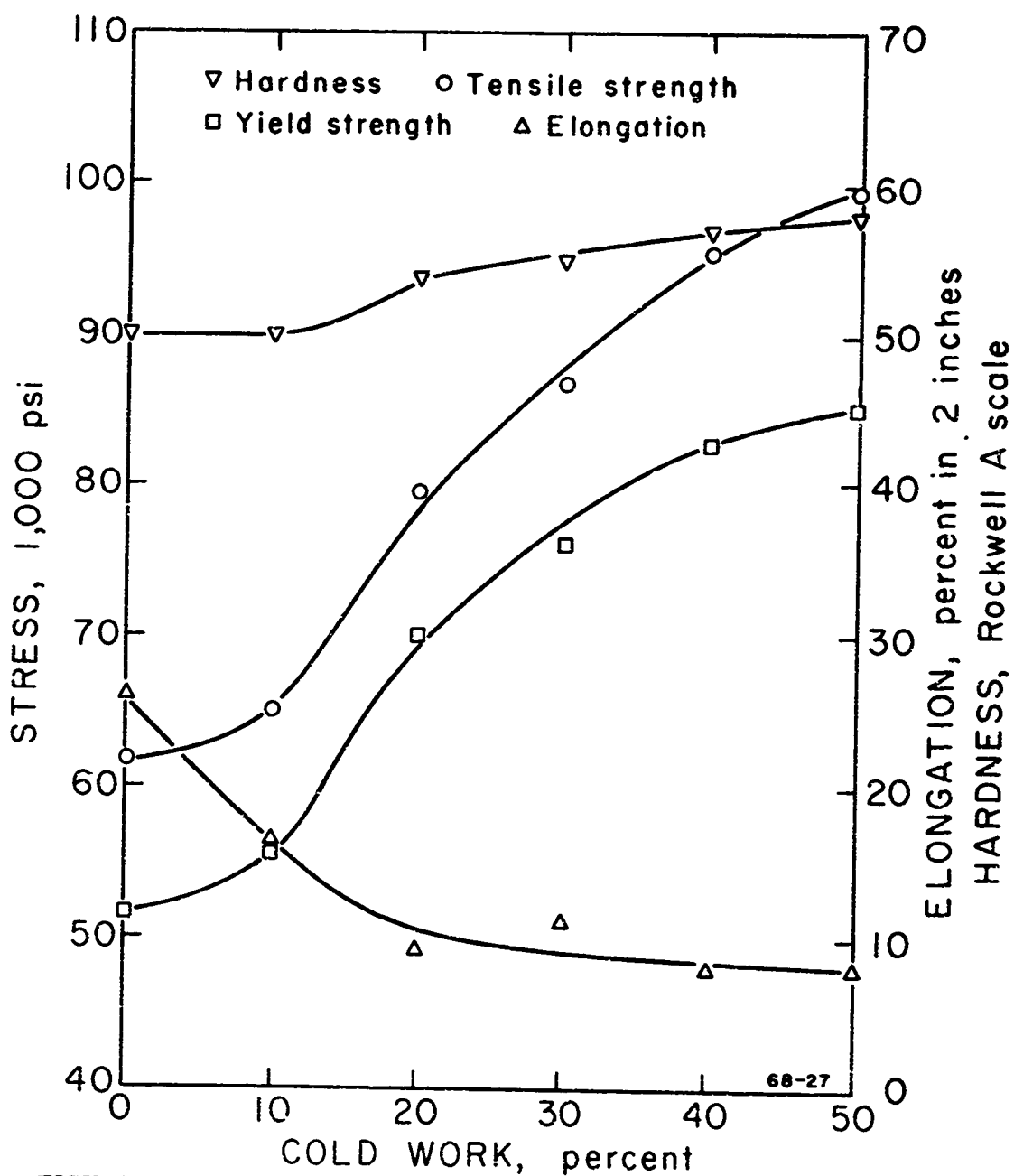


FIGURE 3. - Transverse Tensile Properties and Hardness of 1/16-inch-thick Sheet, Electroslag Melted

The tensile properties of products prepared from electroslog-melted ingots compare very favorably with those prepared from vacuum-arc-remelted ingots and appear acceptable.

Bend Tests:

The room-temperature minimum bend radius was determined for sheet in the as-hot-rolled condition, and sheet reduced 50 percent by cold rolling. Specimens were 2-1/2-inches long, 1/2-inch wide, and 1/16-inch in thickness. The specimens were bent in a fixture with a 1-inch span between the supports. Bending rate was 0.2 inches per minute of punch travel. The radius of the punch was increased successively until no evidence of failure could be detected on the tension side of the specimen after a 90° bend angle. The bent specimens were examined for failure at a magnification of 10. Results are listed in table 4 for both longitudinal and transverse specimens. The bend axis was perpendicular to the rolling direction for longitudinal specimens and parallel to the rolling direction for transverse specimens.

The bending character at room temperature appears to be superior for vacuum-arc-melted material, especially for the hot-rolled sheet. The difference in bend ductility indicated for the two materials might have resulted from ingot preparation before forging. Ingots obtained by vacuum arc melting were machined. Electroslog-melted ingots were not.

TABLE 4 . - Minimum bend radius for 1/16-inch sheet specimens
tested at room temperature

<u>Material</u>	<u>Condition</u>	<u>Orientation</u>	<u>Minimum bend radius</u> ^{1/}
Vacuum-arc remelted	Hot-rolled	Longitudinal	1t
		Transverse	2t
	Cold-rolled 50 percent	Longitudinal	4t
		Transverse	5t
Electroslag- melted	Hot-rolled	Longitudinal	3t
		Transverse	3t
	Cold-rolled 50 percent	Longitudinal	5t
		Transverse	>4t

^{1/} Minimum bend radius was defined as the minimum radius, expressed in units of sheet thickness (1/16-inch,) of the mandrel around which the sheet was bent to a full 90° bend angle without evidence of failure when observed at a magnification of 10 diameters.

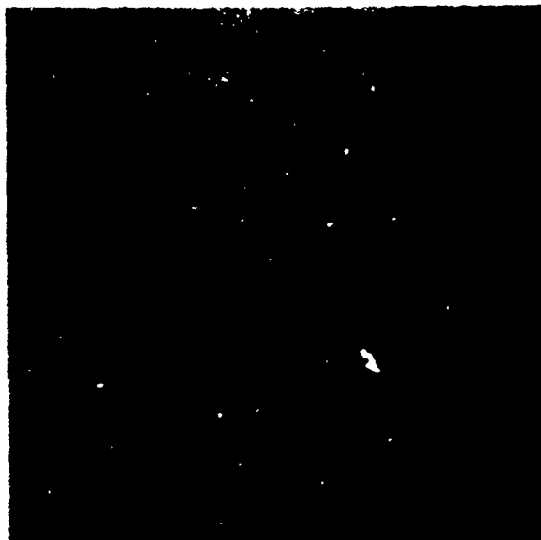
Microstructures:

The structures of electroslag- and arc-melted titanium in the as-rolled condition are shown in figure 4 A + B. The essential difference is the presence of more inclusions in the material consolidated by electroslag melting. After annealing at 700° C for one hour, the structures developed are shown in figure 5 A + B. The alpha-annealed material was cold-rolled to a reduction of 50 percent in thickness. The resultant structures are shown in figure 6 A + B. Attempts to identify the inclusions shown in the photomicrographs by electron-microprobe analysis were not successful; however, the possibility of the inclusions being fluorides or carbides was eliminated. Fluoride inclusions which were revealed with the electron microprobe in the structures of all electroslag-melted material examined are not resolved in the microstructures as shown in figures 4 - 6.

The structures of the annealed plate, shown in figure 5 B, show very little transformed beta, while the hot-rolled sheet, figure 4 B, has appreciable amounts. The final working temperature was apparently close to the alpha-beta transus. Grain size is essentially the same for similar shapes fabricated from ingots melted by the two processes.

Alloy Experience

Two 4-inch-diameter ingots of each alloy — titanium-6 percent aluminum-4 percent vanadium, and titanium-8 percent manganese — were examined for retention of alloying constituents and segregation. One electrode of each alloy



A. As-polished Vacuum-Arc Remelted



A. As-polished - Electroslag

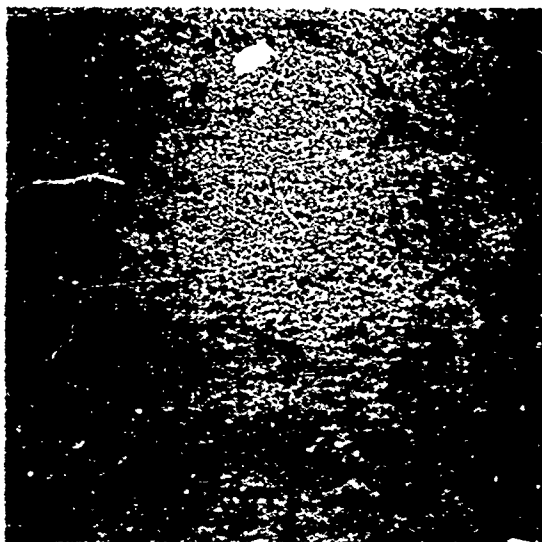


**B. As-polished and Etched -
Vacuum-Arc Remelted**

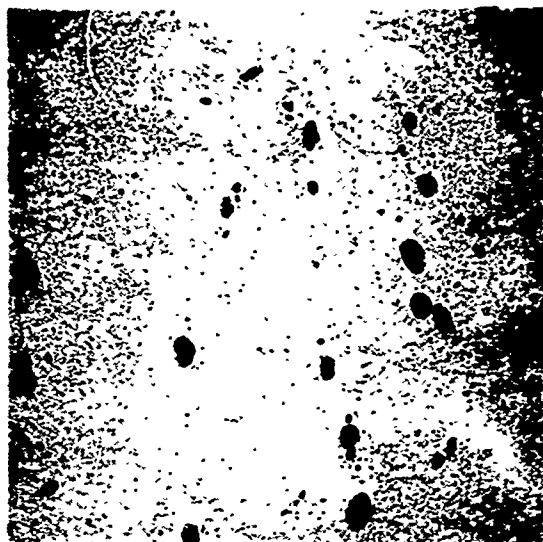


B. As-polished and Etched - Electroslag

FIGURE 4. - Structures of Hot-rolled Sheet 250X



A. As-polished - Vacuum-arc Remelted



A. As-polished - Electroslag

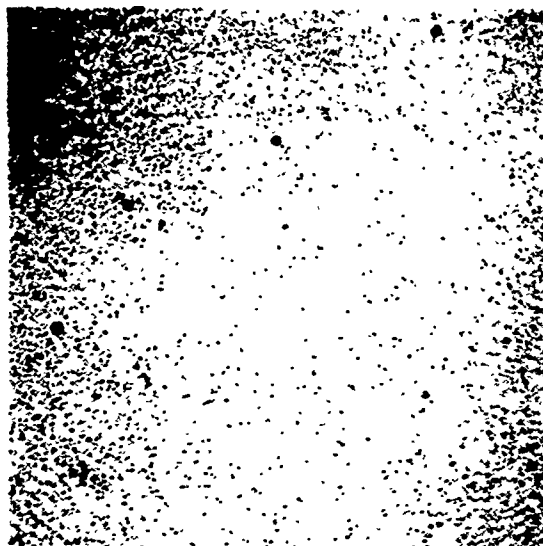


B. As-polished and Etched,
Vacuum-arc Remelted

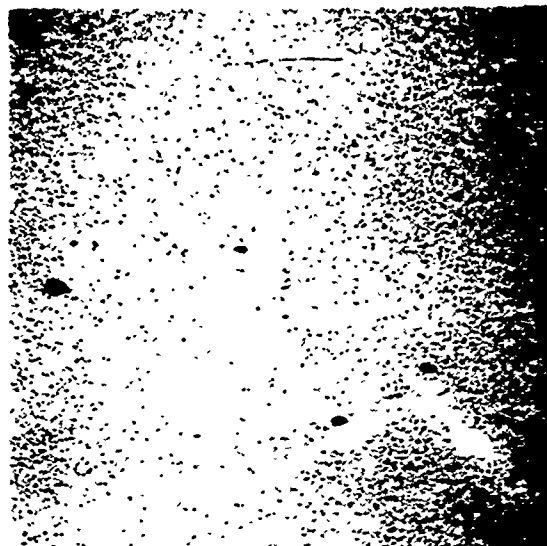


B. As-polished and Etched - Electroslag

FIGURE 5. - Structures of Hot-rolled Plate Annealed at 700° C for 1/2 Hour



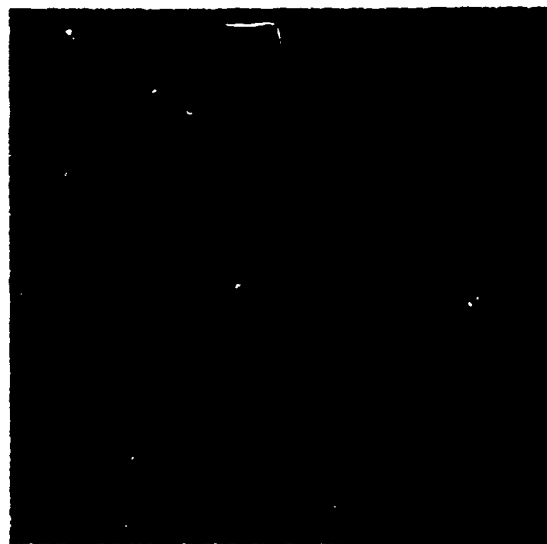
A. As-polished - Vacuum-arc Remelted



A. As-polished - Electroslag



**B. As-polished and Etched -
Vacuum-arc Remelted**



B. As-polished and Etched - Electroslag

**FIGURE 6. - Structures of Sheet Reduced 50 Percent by Cold Rolling
From the Alpha-annealed Condition, 500X**

was forged alloy bar stock, and the other electrodes were of pressed sponge containing the alloying addition as small pieces of aluminum, vanadium, or manganese. The ingots were melted in one-third atmosphere of helium with straight-polarity direct current. The flux was treated, reagent-grade calcium fluoride. Melting was accomplished with 4,500 amperes and 20 to 22 volts. Ingot SA 25,887, a titanium-6 percent aluminum-4 percent vanadium alloy melted from forged bar stock, was analyzed for aluminum content by the atomic absorption method, for vanadium content by a wet method, and for both aluminum and vanadium content by direct reading spectrographic analysis. Nine samples were machined from the ingot: one at the surface, one just below the surface, and seven samples at different locations within the ingot. The ingot was sparked in 25 locations for spectrographic analysis. The results are shown in table 5. Analyses of the electrode for this melt averaged 6.43-percent aluminum and 4.00-percent vanadium. Considering the accuracy of the analytical methods, the average values of aluminum and vanadium for both electrode and ingot indicate the retention of the alloy constituents to be excellent. Furthermore, little alloy segregation is evident. An impurity analysis made for this ingot revealed a slight increase in the concentrations of iron, manganese, and silicon from top to bottom of the ingot.

Ingot SA 25,928, a titanium-6 percent aluminum-4 percent vanadium alloy, was prepared by electroslag melting a pressed sponge electrode containing small pieces of aluminum and vanadium uniformly distributed through-

TABLE 5. - Analyses obtained for ingot SA 25,887, Ti-6Al-4V alloy
electroslag melted from forged bar stock

<u>Aluminum, percent</u>		<u>Vanadium, percent</u>	
<u>Atomic ^{1/} absorption</u>	<u>Spectrographic ^{1/}</u>	<u>Wet Chemistry ^{1/}</u>	<u>Spectrographic ^{1/}</u>
6.20 ^{2/}	6.1	3.91 ^{2/}	3.8
6.25 ^{3/}	6.4	3.89 ^{3/}	4.0
6.79	6.6	3.88	4.1
5.92	6.3	3.80	3.9
6.25	6.4	3.84	3.6
6.38	6.4	3.84	4.1
6.63	6.4	3.80	4.0
6.40	6.3	3.86	3.8
6.63	6.3	3.90	3.8
	6.7		3.9
	6.4		4.2
	6.2		3.6
	6.5		3.7
	6.3		4.0
	7.2		4.2
	6.4		4.1
	6.2		3.8
	6.0		3.6
	6.5		3.6
	6.8		4.1
	6.0		3.5
	6.1		3.8
	5.9		3.8
	5.9		3.8
	6.4		4.0
6 38 Average	6 35	3.86	3 87

^{1/} Accuracy for both the atomic absorption and wet chemistry methods is ± 3 percent of the amount present. Accuracy for the direct reading spectrographic method is ± 5 percent of the amount present.

^{2/} Sample from surface of ingot.

^{3/} Sample from just beneath surface of ingot.

out the electrode. The ingot was analyzed by the direct reading spectrographic method to obtain the results shown in figure 7. The average values were 5.84-percent aluminum and 4.08-percent vanadium, indicating no significant loss of the alloying additions. Within the accuracy of the analytical methods, the ingot was homogeneous.

Titanium-manganese alloy ingots, SA 25,923, melted from a forged bar electrode containing 7.5-percent manganese, and SA 25,932, melted from pressed sponge containing pieces of manganese totaling 8 percent, were also analyzed by the direct reading spectrographic method. The results are shown in figures 8 and 9. For both ingots it appears that some manganese was lost during melting, the average manganese contents being 6.05 percent for ingot SA 25,923, and 7.00 percent for ingot SA 25,932. In both ingots, but especially in SA 25,932, the ingot melted from a sponge electrode, the manganese content was higher near the surfaces of the ingot. The macrostructure of ingot SA 25,932 revealed banding which has been attributed to manganese segregation in arc-melted ingots. The macrostructure of this ingot is shown in figure 10. Improved melting techniques or improved methods of adding the manganese appear necessary before homogeneous ingots of the titanium-8 percent manganese alloy can be prepared by the electroslog melting process.

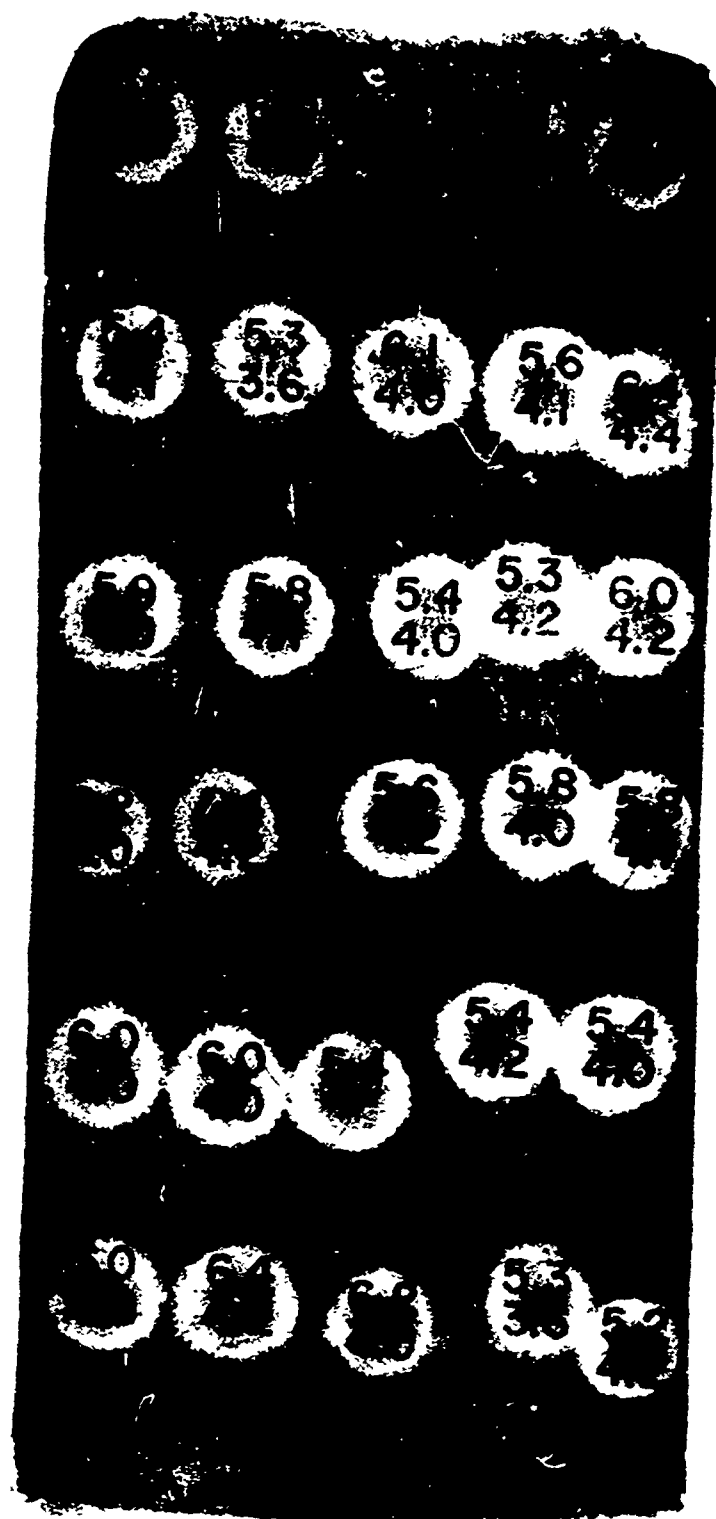


FIGURE 7. - Distribution of Aluminum and Vanadium, in Percent, Ingot SA 25,928

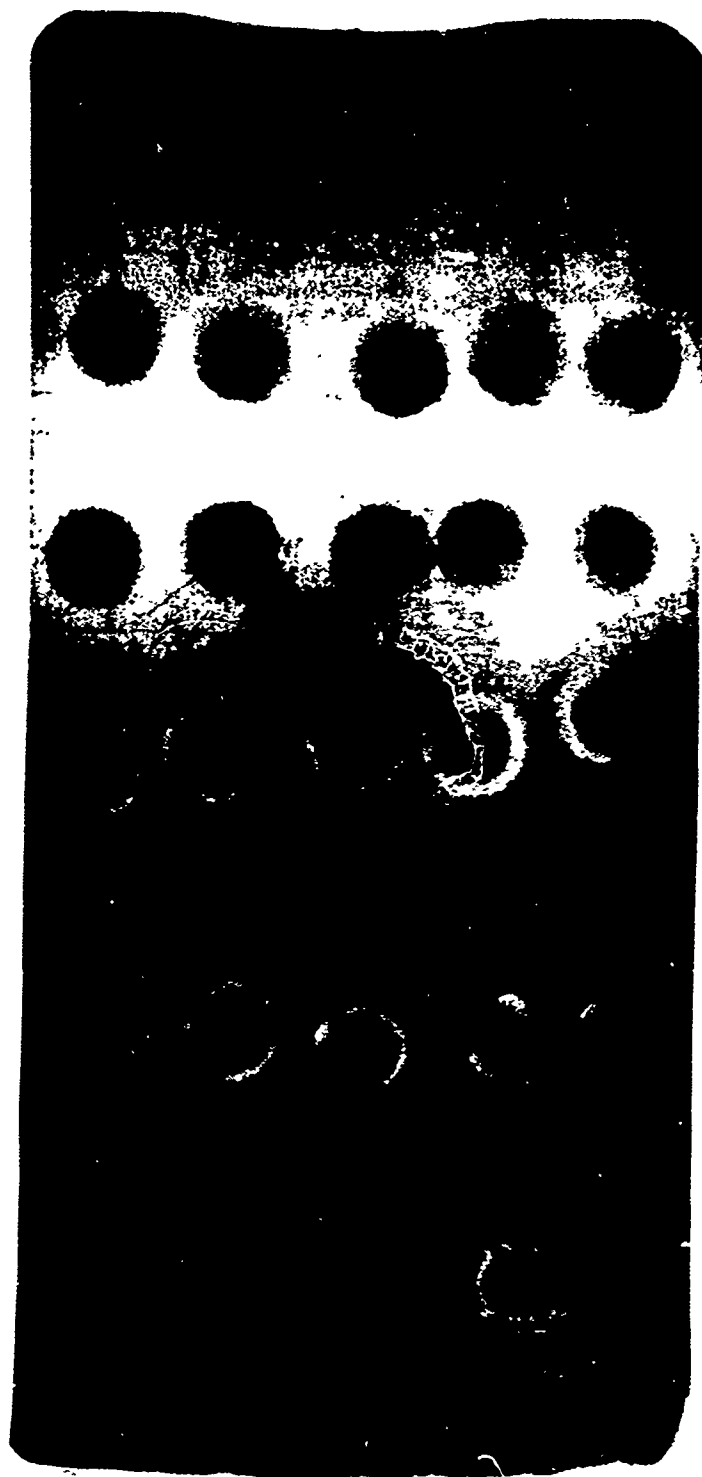


FIGURE 8. - Distribution of Manganese, in Percent, Ingot SA 25,923

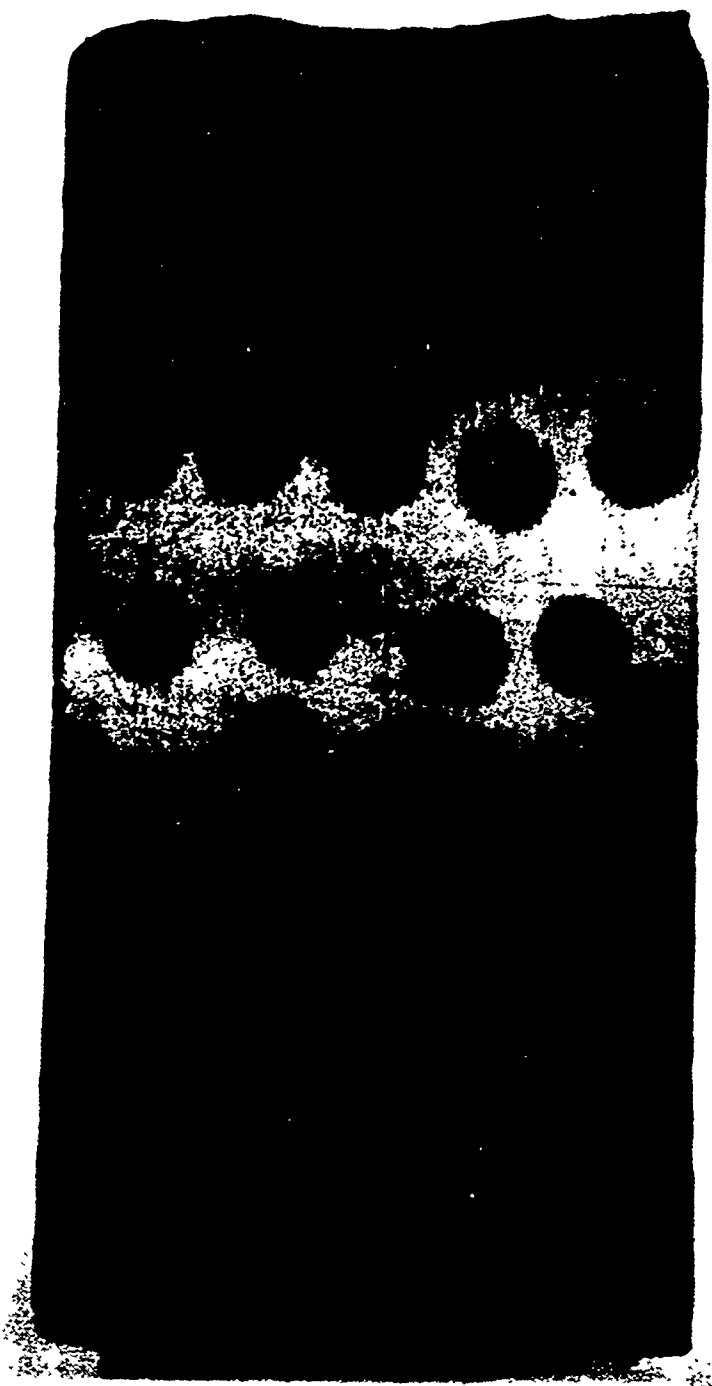


FIGURE 9. - Distribution of Manganese, in Percent, Ingot SA 25,932



**FIGURE 10. - Titanium-8% Manganese Ingot Section Single Electroslag Melted
From Electrode of Sponge and Manganese Metal**

Alternate Schemes

Alternate Power Sources and Furnace Atmospheres:

Alternating current and reverse-polarity direct current (electrode positive) were studied as alternate power sources for preparing 4-inch-diameter electroslag-melted titanium ingots. Evaluation was made by comparing melting characteristics and ingot impurity content with that established for melting with straight-polarity direct current. Six ingots were melted: three with alternating current and three with reversed-polarity direct current. Treated reagent-grade calcium fluoride and vacuum-distilled sponge were used to prepare all of the ingots. The ingots weighed about 17 pounds each.

Two of the ingots prepared with alternating current were melted in a closed furnace containing one-third atmosphere of helium. The other was prepared with helium flowing through the furnace chamber at a rate of 12 cubic feet per minute. The ingots prepared with reversed-polarity direct current were melted with either a closed furnace containing one-third atmosphere of helium, a furnace with 4 cubic feet per minute of helium flowing through the chamber, or with the furnace opened to admit air.

Smoothness of operation during ac melting was about the same as determined for electroslag melting with straight-polarity direct current. Both current and voltage requirements for good ingot sidewalls were slightly higher with alternating current than with straight-polarity direct current. The melting

rate was slowest with alternating current and highest with reversed-polarity direct current. Typical values to produce good ingots, as judged by appearance, follow:

	<u>dc-straight polarity</u>	<u>dc-reversed polarity</u>	<u>ac</u>
Melting rate, lbs/min	2	2-1/3	1-1/3
Current amperes	4500	4900	5000
Potential volts	22	25	24
Power utilization, kw-hr/lb	0.8	0.9	1.5
Optimum slag cover, inches	1-1/2 to 2	1-1/2 to 2	1-1/2 to 2

There was a noticeable difference in the adherence of sidewall slag to the ingots prepared by the different currents. The sidewall slag was much easier to remove from the ingots prepared with alternating current and actually fell off of the ingots prepared with reverse-polarity direct current.

Each ingot was sampled near the top and near the bottom. Impurity analyses determined for the samples are shown in table 6. Included in the table for comparison are analyses for ingots melted with straight-polarity direct current in a closed furnace containing one-third atmosphere helium, a furnace with helium flowing through the chamber, and a furnace opened to admit air.

In general, the analyses show very little difference in the impurity contents for ingots prepared with a helium atmosphere, either static or flowing. It appears that the polarity of the current for melting does not have a marked effect on ingot chemistry. For ingots melted with air admitted to the furnace

TABLE 6. - Analyses ^{1/}for electroslag-melted ingots prepared with different power sources and furnace atmospheres. All values in parts per million.

Ingot number	Melting condition	Sample location	O		H		F	C	N	Al	Fe	Mg	Si	Sn
			Edge	Center	Edge	Center								
SA 26, 264	ac-power	top	869	817	29	25	90	90	47	50	500	50	100	400
	static helium	bottom	1436	922	22	18	80	93	49	50	400	20	100	300
SA 26, 265	ac-power	top	799	911	22	27	90	94	55	<50	500	20	100	<180
	static helium	bottom	1332	1196	28	24	100	104	59	50	500	20	100	<180
SA 26, 267	ac-power	top	448	697	18	15	130	101	63	<50	400	20	100	<180
	flowing helium	bottom	1340	802	11	13	100	84	60	<50	400	20	100	<180
SA 26, 273	reversed polarity top		836	711	30	25	140	91	54	<50	500	50	100	250
	static helium bottom		655	678	23	26	100	111	42	<50	500	50	150	250
SA 26, 274	reversed polarity top		678	676	22	21	100	98	56	<50	400	50	100	250
	flowing helium bottom		547	669	30	26	110	89	68	<50	800	30	100	250
SA 26, 275	reversed polarity top		1125	759	26	24	200	71	1690	200	300	80	400	600
	air bottom		546	799	22	21	220	75	246	<50	200	30	100	<180
SA 25, 897	straight polarity top		748	752	18	17	90	86	66	<50	400	80	200	<180
	static helium bottom		1150	836	17	12	80	183	78	100	200	80	250	<180

(Continued)

TABLE 6. - Analyses^{1/} for electroslag-melted ingots prepared with different power sources and furnace atmospheres. All values in parts per million. (Continued)

Ingot number	Melting condition	Sample location	O		H		F	C	N	Al	Fe	Mg	Si	Sn
			Edge	Center	Edge	Center								
SA 25, 975 ^{2/}	straight polarity	top	517	398	186	201	140	70	104	100	400	85	<100	<180
	flowing helium	bottom	928	720	195	197	60	85	105	100	400	50	<100	<180
SA 26, 084	straight polarity	top	2330	3270	19	18	130	692	420	50	300	80	300	300
	air	bottom	1470	1790	21	18	100	115	856	50	300	30	200	<180

^{1/} See Table 1, Footnote 1, for analytical methods.

^{2/} Ingot No. SA 25, 975 prepared from water-leached sponge (note hydrogen content.)
All other ingots prepared from vacuum-distilled sponge.

NOTE: Ca, Cr, Mn, V, Mo all 50 or <50 ppm.

All ingots -- Ni = <35 ppm

Pb = <200 ppm

chamber, contamination by oxygen and nitrogen is indicated. It appears that straight-polarity melting results in more contamination of the ingots than for ingots melted with reversed-polarity. However, before a general statement can be made, additional melts made in air and with reverse-polarity direct current should be evaluated.

Electroslag Melting of Scrap:

One electrode, prepared from scrap turnings, was electroslag melted into an ingot 4 inches in diameter. The turnings had been machined from a titanium-6 percent aluminum-4 percent vanadium alloy. The turnings were cleaned before pressing into bars 2-inches by 2-inches in cross section and 10-inches long. The electrode was melted with 4,500 amperes direct current at 23 volts. Treated reagent-grade calcium fluoride was used for the slag. Melting characteristics were no different from those for melting sponge or forged bar electrodes.

The resulting ingot had smooth sidewalls free of surface defects. Analysis of the ingot showed a 5.7-percent aluminum content and a 4.0-percent vanadium content. Metallic impurities were considerably higher than for ingots prepared from sponge, which is not unusual for scrap melted by other methods. The values in ppm are listed below:

Ca - - - - -	<50	Mo - - - - -	400
Cr - - - - -	5000	Ni - - - - -	50
Cu - - - - -	100	Pb - - - - -	<200
Fe - - - - -	1000	Si - - - - -	1500
Mg - - - - -	30	Sn - - - - -	600
Mn - - - - -	600		

Oxygen, hydrogen, and nitrogen were not determined.

Although sound ingots with good surfaces can be prepared by electroslag melting pressed turnings, it is doubtful that adequate purity would be obtained unless the turnings were carefully sorted and cleaned before melting.

Electroslag Melting of a Columbium Alloy:

One 4-inch-diameter ingot of a columbium alloy containing 10-percent titanium and 5-percent zirconium was prepared by electroslag melting an electrode of forged bar stock. The electrode was 1-1/2 inches by 1-1/2 inches square. The slag was the eutectic composition of zirconium and yttrium oxides (20% ZrO_2). This slag had been used for molybdenum with some success. Of the 1.4 kilograms of slag charged to the furnace hopper, 1.2 kilograms were fed into the crucible for melting.

The furnace was charged with the electrode and 80 grams of starting base, evacuated, and backfilled with helium to a pressure of one-third atmosphere. Melting was started with arc conditions of 1,000 amperes straight-polarity direct current and 20 volts. The power was raised as the slag was added. A quiet melting condition was obtained with 5,000 amperes and 16 volts. Sidewalls of the resulting ingot were not good. This is indicated to a certain extent in the macrograph of figure 11. The slag adhered tightly to the ingot.

The shrinkage cavity and porosity at the top of the ingot resulted from not hot-topping. This clearly demonstrates the importance of the hot-topping operation. Grain size of the ingot was relatively fine, as shown in the macro-etched section.



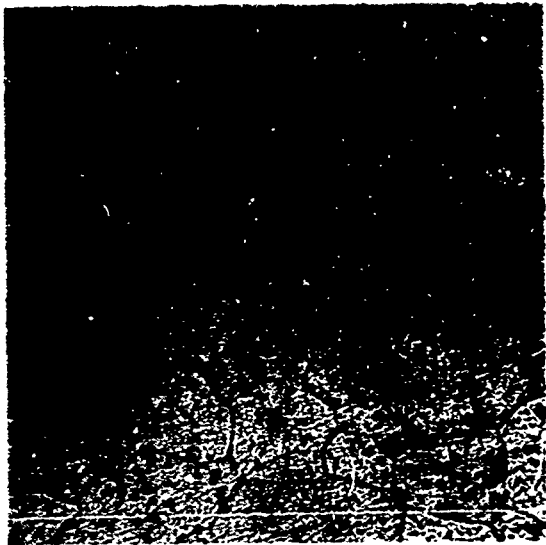
FIGURE 11. - Macroetched Section of Electroslag-melted Columbium-
10% Titanium-5% Zirconium Alloy. SA 26,023

Before melting, the alloy contained 490 ppm of oxygen. Melting increased the oxygen content to 2,680 ppm at the center of the ingot, and 3,040 ppm near the top. Yttrium content of the ingot was between 0.1 and 1 percent. Other metallic impurities were the same as for the electrode. The slag did pick up at least 3-percent titanium.

Microstructures of the electrode and ingot are shown in figure 12. The small black particles that appear dispersed along subgrain boundaries are assumed to be oxides.

Brinell hardness of the ingot, measured on the cut surface, averaged 230. The electrode hardness was 185 Brinell. The increase in hardness is attributed to the increase in oxygen content during melting. Brinell hardness measurements made along the unmelted portion of the electrode showed an increase in hardness from 185 to 250 as the melted end was approached.

As only one melt was made and then with only one slag composition, conclusions concerning the electroslag melting of columbium or columbium alloys are hardly in order. However, indications are that oxide contamination will occur if oxide slags are used, at least when zirconium and titanium-alloy additions are involved.



Electrode Stock



Longitudinal Section of Ingot

**FIGURE 12. - Microstructures of Columbium-10 Percent Titanium-5 Percent Zirconium Alloy Before and After Electroslag Melting
250X**

Bifilar Melting

Russian research on the use of the "bifilar" or 2-electrode electroslag melting has been reported (19) as an effective means of melting slab-shaped ingots. Attempts were made to utilize this melting technique for preparing small-scale, slab-shaped titanium ingots. In this melting scheme, the furnace was equipped with two electrodes, and the melting current was maintained between these two electrodes rather than from the electrode to the crucible bottom as in conventional electroslag melting. One advantage claimed was that this technique eliminated breakdown of the slag cover between the ingot and the crucible wall and the resulting defects in the ingot structure. An additional advantage would be more even distribution of heat over the cross section of a rectangular ingot.

For the tests conducted, a small arc furnace was modified by installing two electrodes through the furnace top in place of the usual single electrode. Each of the electrodes was connected to one side of an ac power supply, and the slab-shaped crucible into which the electrodes extended was grounded. Both electrodes were driven by a common electrode drive; provisions were not made for control of the individual electrode position. Melting was conducted at one-third of an atmosphere of helium, and the calcium fluoride slag was added to the melting zone as a solid.

Numerous variations of starting procedures, electrode spacing and configuration, methods of slag additions, and electrode control procedures were tried in an attempt to melt by this technique. All runs were terminated before a full pool of molten slag was formed because of uneven melting of the two electrodes. In most runs, one or the other of the electrodes did not melt at all or only very slightly. The electrode that did not melt froze into the pool of metal as the pool formed, and the other electrode was consumed rapidly until the end was above the slag. Because one of the electrodes was not melted, it was impossible to continue feeding the two electrodes downward, and the run had to be terminated.

Examination of the contents of the crucible following each run indicated that as soon as a portion of the slag was melted a pocket of molten slag formed about one electrode. This pocket of molten slag was not in contact with both electrodes; consequently, uneven melting of the two electrodes took place. The electrode not in contact with the molten pool of slag was consumed rapidly because of arcing between this electrode and the surface of the slag. This condition existed until the end of one electrode was against the bottom of the crucible, and the other was too short to reach the slag.

It is possible that individual control of the two electrodes might have overcome this difficulty. A more practicable solution would have been provision for the addition of liquid slag to initiate the run; however, both ideas were considered to be beyond the scope of this work.

THE PROTOTYPE FURNACE

One of the purposes of this research was to produce slab-shaped ingots of sufficient size to establish the suitability of electroslag melting for the production of ingots on an industrial scale. A comparative evaluation was to be made of slab-shaped ingots produced by electroslag melting titanium sponge from different sources and of slab-shaped ingots produced by vacuum arc melting. A furnace, capable of both vacuum arc melting and electroslag melting, was built for producing slab-shaped ingots with a 7-inch by 20-inch cross section. These dimensions for the ingot cross section were an arbitrary compromise between the large scale desired to verify the adaptability of the process to industrial scale and the limitation imposed by the available power supply for melting. Provisions were also made for melting ingots with a circular cross section as large as 12 inches in diameter.

Figure 13 is a cross section of the furnace, and figure 14 is an overall view of the installation. The furnace chamber was constructed of three mild-steel tubular sections. The lower section, which houses the crucible, was 30 inches in diameter and 60 inches long. The middle section was also 60 inches long but only 24 inches in diameter and was equipped with access doors. Both the middle and the lower sections were mounted on a trolley and could be rolled forward from under the furnace platform for loading and unloading the furnace. The short (14-inches long) upper section of the furnace was

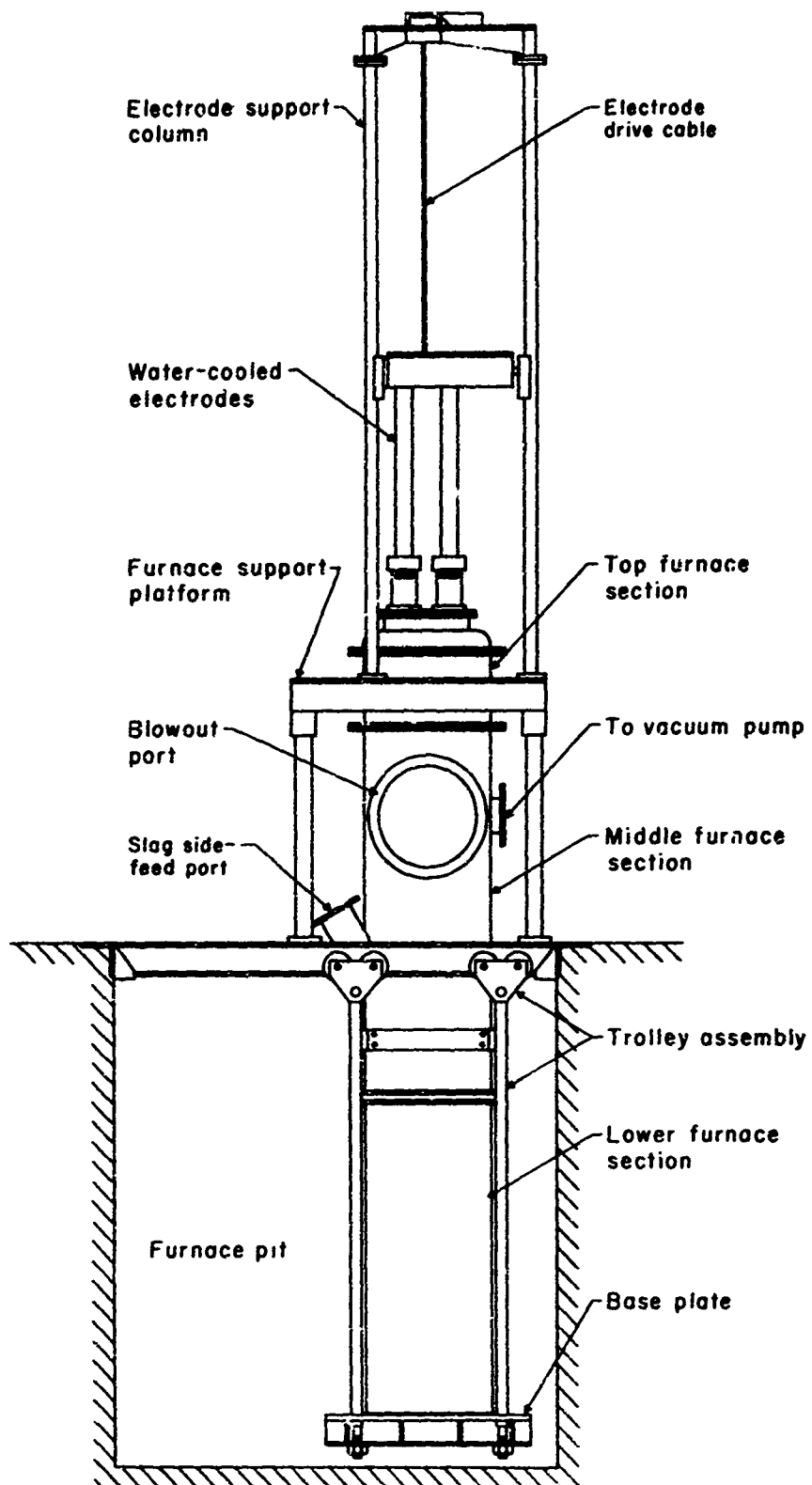


FIGURE 13.-Prototype Furnace for Electroslag Melting Titanium.

68-2742

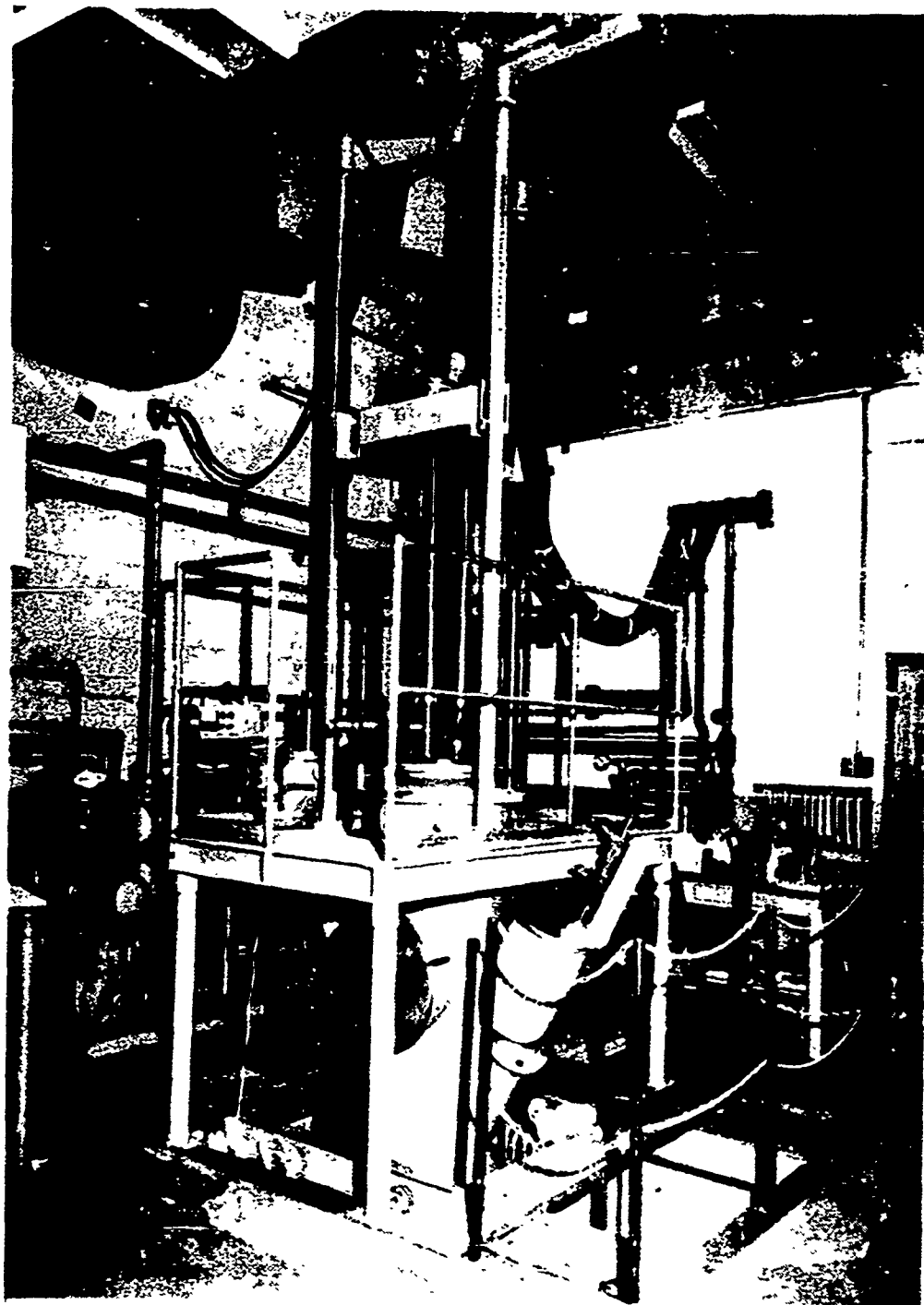


FIGURE 14. - Prototype Furnace

mounted directly to the platform. This platform also supported a tripod which carried the electrode drive and alignment mechanism.

Not shown in figure 13 but visible in figure 14 at the front of the furnace is an auxiliary tank for sidefeeding granular slag during melting. It can also be seen in figure 14 that the lower portion of the furnace was below floor level to provide the required headroom. The furnace was equipped with an optical system for remote viewing during melting.

The vacuum system, which was connected to the rear side of the middle furnace section, consisted of a 100 CFM mechanical pump for roughing the chamber and a 1,250 CFM blower backed by a 140 CFM mechanical pump for attaining the ultimate vacuum. This system provided an ultimate vacuum of less than 10 microns.

The crucible for producing 7-inch by 20-inch, slab-shaped ingots is shown in figure 15. This crucible was divided into four sections: two flat sections, each 14-inches wide, for the sides, and two curved end pieces. The corners of the end pieces were curved to a 1-1/2-inch radius on the inside surface. Each of these four sections and the water-cooled copper bottom for the crucible had its own water-cooling circuit. As can be seen in figure 15, inlet and outlet water lines were provided for each section through the bottom plate of the furnace chamber. The crucible sections were bolted together with a simple, metal-to-metal joint; no bolted vacuum-tight joints were required

other than those on the water supply lines. The crucible section shown in figure 15 was 30-inches long. Provisions were made to bolt similar sections to the top of the sections shown for making longer ingots.

Figure 16 shows the water jacket and crucible assembly used to produce round ingots in the prototype furnace. This assembly can be used to produce ingots 12 inches in diameter and 48 inches long.

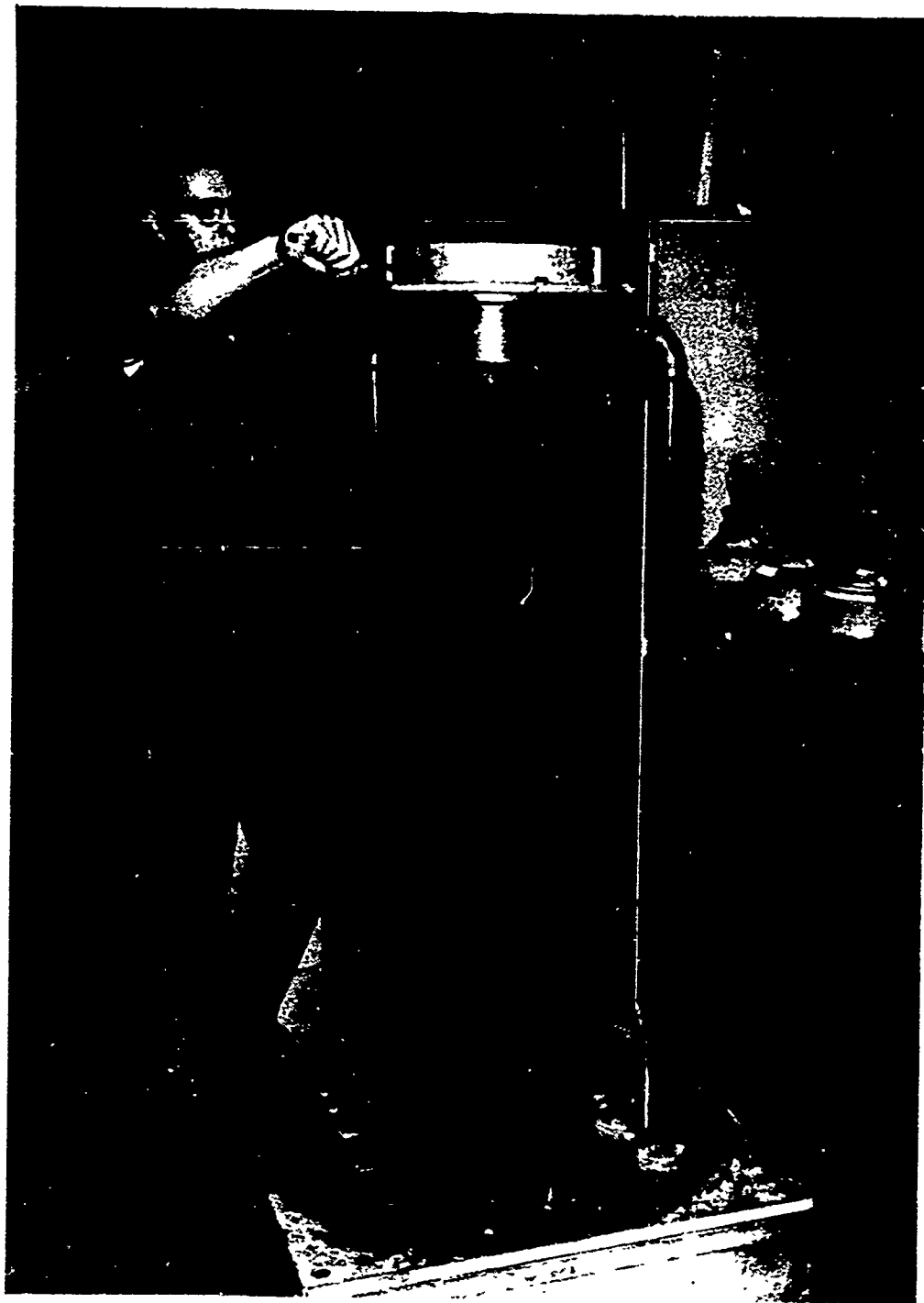
Melting Experience in the Prototype Furnace

The prototype furnace was used in a comparative evaluation of slab-shaped ingots prepared by electroslog melting from domestic, leached-and-dried sponge; vacuum-distilled sponge; and domestic sponge prepared by a proprietary, gas-swept method. A slab-shaped ingot was also prepared from leached-and-dried sponge by vacuum arc melting. Melting procedure for vacuum arc melting did not differ from vacuum arc melting in any other furnace except for use of the slab-shaped crucible. Electroslog-melting procedures as used with the prototype furnace are outlined in the following paragraphs.

For electroslog melting, titanium-sponge electrodes were single melted to produce an ingot. These electrodes were formed by heliarc welding 2-inch by 2-inch by 10-inch compacts of sponge into an electrode with a 4-inch by 16-inch cross section. Figure 17 shows a typical sponge electrode ready for melting.



FIGURE 15. - Crucible for Slab-shaped Ingots



**FIGURE 16. - Crucible and Water-jacket Assembly for Producing
12-inch-diameter Round Ingots**



FIGURE 17. - Electrode of Titanium Sponge for Melting in Slab-shaped Crucible

A pin, usually a 3- to 4-inch length of 2-inch by 2-inch sponge bar machined to a point at the end, was welded to the bottom of the electrode to serve as a starting pin. When the electrode was loaded into the furnace, the electrode was lowered until this pin rested on a starting pad placed in the bottom of the crucible. The starting pad was a 3/4-inch-thick section from a previously melted slab-shaped ingot or a 3/4-inch-thick pad of sponge-metal compacts welded together to cover the bottom of the crucible.

After the electrode was lowered onto the starting pad, the entire charge of calcium fluoride slag needed for melting the ingot was charged into the crucible. The calcium fluoride was treated prior to charging the furnace by the methods outlined below. The furnace was evacuated to the ultimate vacuum of the system and then backfilled to approximately one-third atmosphere with helium.

Melting was started by first operating for 3 to 5 minutes with the electrode dead-short to the starting pad. The power was held to a low value of 3,000 to 4,000 amperes and 2 to 3 volts. The electrode was then raised off the starting pad, and the power was maintained at a value at which the calcium fluoride melted but the electrode did not. As soon as the entire charge of calcium fluoride was molten, the power was increased until the electrode melted at a satisfactory rate.

Results Obtained With Prototype Furnace

One of the primary objectives of research with this furnace was to determine whether satisfactory slab-shaped ingots could be produced by single-melting domestic, leached-and-dried titanium sponge. Leached sponge prepared by both sodium reduction and magnesium reduction were tested. Vacuum-distilled sponge from a foreign source and sponge prepared by a proprietary, gas-swept process were also tested.

Procedures developed for the production of small-scale ingots by a single, electroslog melting step were described in previous sections of this report. These small-scale studies showed that the hydrogen content of the sponge was not reduced during electroslog melting, and, for this reason, leached-and-dried sponge was not considered a satisfactory starting material for producing ingots by electroslog melting. Melting studies with the prototype furnace would not be expected to produce any different results as far as hydrogen content of the metal was concerned. Large-scale tests were conducted, however, to see if large, slab-shaped ingots could be prepared and if these ingots would be suitable for fabrication without surface conditioning.

Variables Noted

During melting studies in the prototype furnace, variables studied included sponge composition, slag depth, electrical parameters, and electrode geometry. In addition, ingots were prepared in the slab-shaped crucible by

both conventional vacuum-arc melting and electroslag melting, and ingots were prepared by electroslag melting in the 12-inch-diameter round crucible. Alloy ingots were prepared in the slab-shaped crucible from electrodes of previously melted bar stock.

The various sponge compositions studied were the same as those studied on small-scale tests. Ingots were prepared from imported, vacuum-distilled sponge, domestic leached-and-dried sponge of both the sodium and magnesium-reduced variety, and from domestic sponge prepared by a proprietary gas-swept method. These ingots were compared with first- and second-melt ingots prepared by conventional vacuum-arc melting.

In electroslag melting, approximately 40 to 50 pounds of calcium fluoride slag were used for each ingot melted in the 7-inch by 20-inch crucible. This provided a minimum slag cover 2-1/2 to 3-inches deep. Inasmuch as the entire charge of slag was added to the crucible prior to the start of melting, the depth of the slag varied slightly as the melt progressed. The depletion of slag cover during any given melt was related to the quality of ingot wall obtained, if a very rough wall was produced, larger amounts of slag were entrapped along the sidewall than if a fairly smooth wall was obtained. No significant difference was noted in the quality of ingot wall from bottom to top of the slab-shaped ingots as a result of decreasing slag depth. However, in several runs when the slag depth decreased much below 2 inches, the voltage drop through the slag cover decreased to a value below that required for satisfactory melting and thus affected sidewall quality.

Table 7 gives pertinent data obtained during melting of ingots in the prototype furnace. Ingots SA 25,824 and SA 25,877 were vacuum arc melted and all others were electrosag melted. It should be noted that total kilowatt-hours, kilowatt-hours per pound, and melting rate are all influenced by total ingot weight. During electrosag melting in the prototype furnace, a certain amount of time was involved in melting the initial charge of slag. Consequently, during melting by this method, the overall efficiency of the operation was less for shorter ingots of a given crucible size.

In general, the electrosag-melting process was less efficient than arc melting; melting rates were lower and power requirements were higher for electrosag melting. When one considers the fact that electrosag melting yields a finished ingot in one melting operation, the electrical efficiencies of the two processes were more comparable, but vacuum arc melting was still more efficient. Expressed in terms of kilowatt-hours per pound, the vacuum-arc-melted ingots required approximately 0.85 kw-hrs/lb for double-melted ingot, and the electrosag-melted ingots required from 0.85 to 2.16 kw-hrs/lb.

Resulting Ingots

The electrosag-melting process as applied to the prototype furnace was unsuccessful to the extent that the process did not yield slab-shaped ingots suitable for direct conversion to sheet or plate. Some machining of the outer surface would be required. The electrosag ingots were, in most cases, sound

TABLE 7. - Data obtained during melting of ingots in prototype furnace

Melt number	Electrode composition	Electrode cross section, inches	Melting technique	Ingot weight, lbs.	Total kw-hrs.	Melting rate, lbs./min.	Nominal melting current, amps.	Nominal arc pot'n., volts
SA 25, 824	Leached and dried magnesium reduced titanium sponge	4 x 16	Vac. arc first melt	513	216	9.87	9,000 - 9,500	29-30
SA 25, 877	Remelt SA 25, 824	3-1/4 x 12	Vacuum arc remelt	463	195	10.8	9,300	32-33
SA 25, 835	Leached and dried magnesium reduced titanium sponge	4 x 16	Electroslag	529	453	5.59	10,500 - 12,000	30
SA 25, 886	Vacuum distilled magnesium reduced titanium sponge	4 x 16	Electroslag	528	1,141	1.97	14,400	20-26
SA 25, 934	Gas-swept magnesium reduced titanium sponge	4 x 16	Electroslag	419	588	4.98	14,500	32
SA 26, 157	Leached and dried sodium reduced titanium sponge	4 x 16	Electroslag	229	258	6.45	13,200	40
SA 26, 253	Vacuum distilled magnesium reduced titanium sponge	3 x 16	Electroslag	465	693	5.31	15,000	30

(Continued)

TABLE 7. - Data obtained during melting of ingots in prototype furnace (Continued)

Melt number	Electrode composition	Electrode cross section, inches	Melting technique ^{1/}	Ingot weight, lbs.	Total kw-hrs.	Melting rate, kw-hr/lb.	Nominal melting current, amps.	Nominal arc pot'n., volts
SA 26, 266	Ti-5Al-2.5Sn forged bar	1-5/8 x 12 ^{2/}	Electroslag	265	517	1.95	4.0	34
SA 26, 282	Ti-6Al-4V forged bar	3-1/4 x 15-3/4	Electroslag	362	736	2.03	4.0	32
SA 26, 297	Gas-swept magnesium reduced titanium sponge	2 x 16	Electroslag	344	500	1.45	4.93	32
SA 26, 457	Gas-swept magnesium reduced titanium sponge	8-inch octagon	Electroslag	645	573	0.89	5.50	30
SA 26, 470	Vacuum distilled magnesium reduced titanium sponge	8-inch octagon	Electroslag	335	667	2.00	3.25	27-28 13,000 - 13,500

^{1/} All ingots were melted in the 7-inch x 20-inch slab-shaped crucible except SA 26, 457 and SA 26, 470 which were melted in a 12-inch-diameter round crucible.

^{2/} Electrode was offset in crucible to provide equal spacing on 3 sides with wider spacing; on fourth side.

internally and were superior in this respect to vacuum-arc-melted ingots prepared in the slab-shaped crucible. Considerable subsurface porosity was noted near the sidewalls of the arc-melted ingots. However, no attempt was made to improve operating parameters for arc melting, and it is not known if better arc-melted ingots could be prepared as a result of more carefully established melting conditions. This same reservation should also apply to electrosag ingots, since the number of these melted was not great.

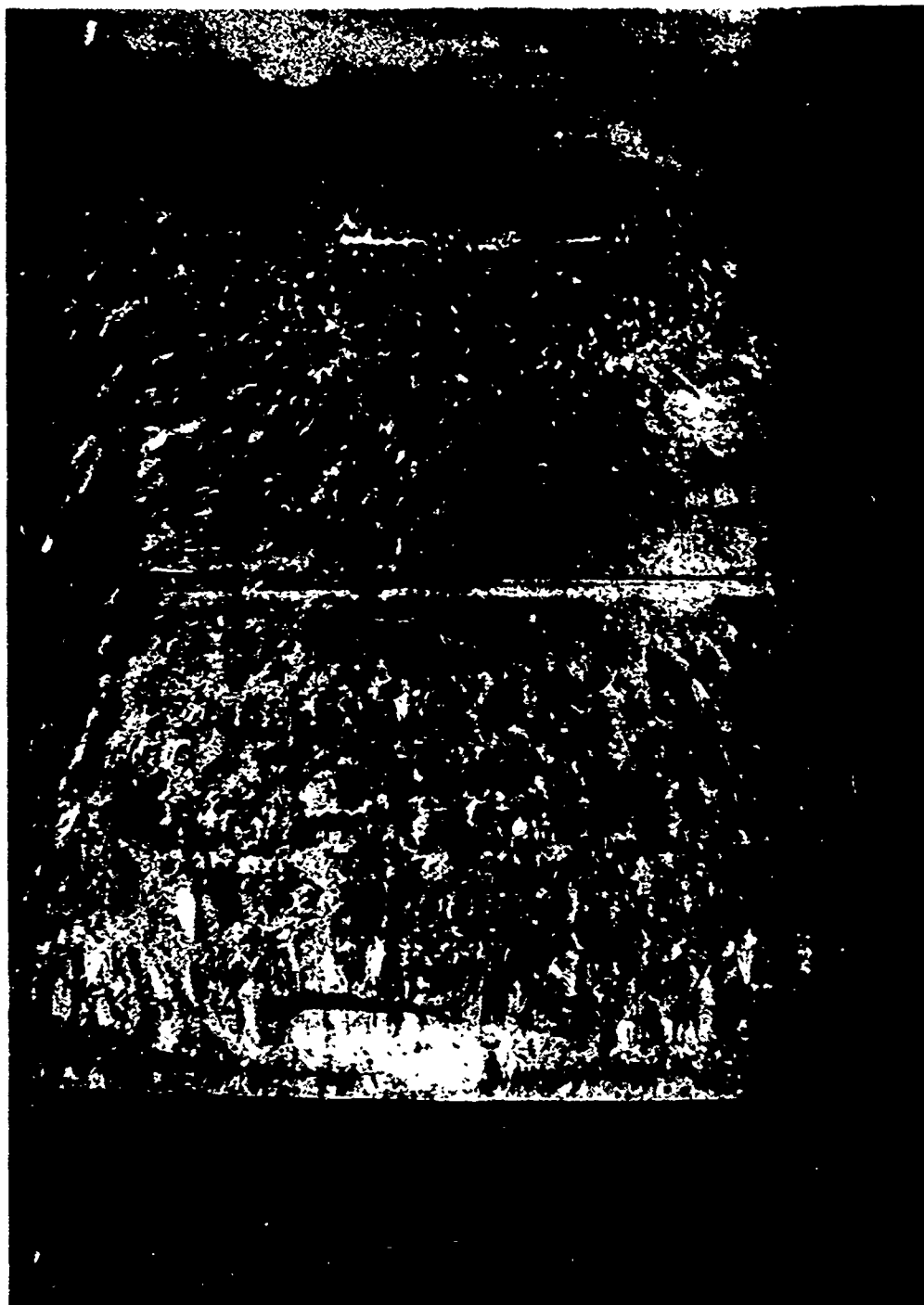
Figure 18 shows an ingot (SA 25, 835) prepared by electrosag melting, and figure 19 shows the internal structure of this same ingot. Starting material for this ingot was leached-and-dried titanium sponge prepared by magnesium reduction. Figure 20 shows the internal structure of an ingot prepared from this same sponge by double vacuum-arc melting in the slab-shaped crucible. Considerably more subsurface porosity is evident in the ingot prepared by vacuum-arc melting.

No significant differences were noted in the impurity content of ingots produced in the prototype furnace and ingots prepared in the small-scale tests. Analyses of representative ingots from the prototype furnace are included in table 8. The same general trends were noted with regard to hydrogen and fluorine contamination for ingots from the prototype furnace as for small-scale ingots.

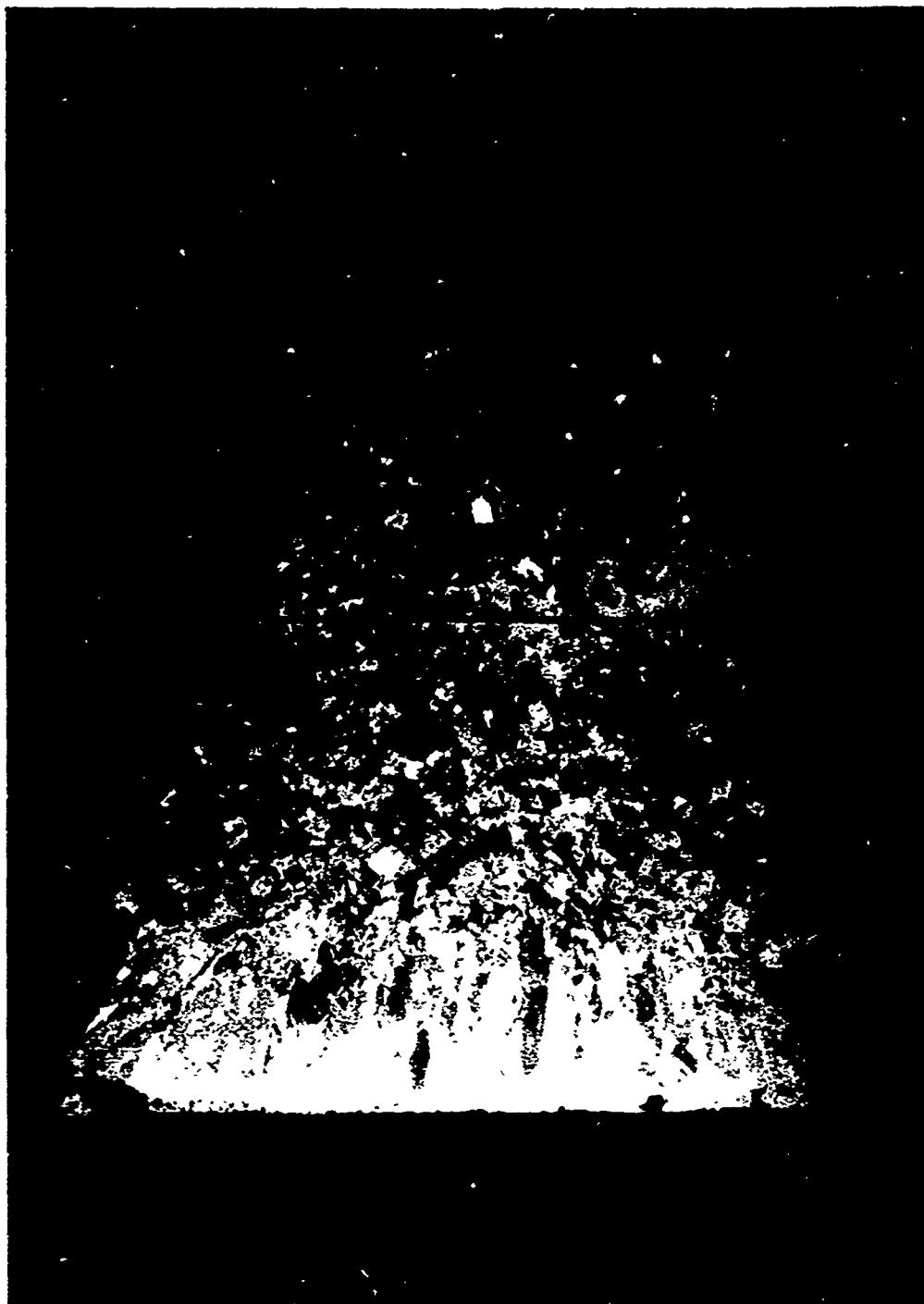
One trend which was more noticeable in the large-scale, slab-shaped ingots was an increase in hardness at the bottom of the ingots. The hardness



**FIGURE 18. - Slab-shaped Ingot SA 25, 835 Prepared by Electroslag Melting
Leached-and-dried Titanium Sponge**



**FIGURE 19. - Etched Internal Surface of Ingot SA 25,835 Prepared by Electroslag
Melting Leached-and-dried Titanium
Sponge**



**FIGURE 20. - Etched Internal Surface of Ingot SA 25,877 Prepared by Double
Vacuum-arc Melting Leached-and-dried Titanium
Sponge**

TABLE 8. - Analyses of slab-shaped ingots melted in the prototype furnace

Ingot	Description	Sample location ^{1/}	Impurity content, ppm				
			C	N	O	H	F
SA 25, 824	Vacuum arc first-melt leached and dried titanium sponge	Top	74	2/	2/	2/	2/
		Middle	84	66	706	34	2/
		Bottom	119	2/	2/	2/	2/
SA 25, 877	Vacuum arc remelt of SA 25, 824	Top	81	75	816	19	2/
		Middle	79	57	823	18	2/
		Bottom	88	67	771	19	2/
SA 25, 835	Electroslag-melt leached and dried titanium sponge	Top	55	60	734	190	2/
		Middle	51	61	766	180	2/
		Bottom	232	69	853	189	2/
SA 25, 886	Electroslag-melt vacuum distilled titanium sponge	Top	83	32	527	38	200
		Middle	63	38	533	9	240
		Bottom	56	48	676	25	180
SA 25, 934	Electroslag-melt gas-sweep processed titanium sponge	Top	82	112	615	58	180
		Middle	71	125	695	63	120
		Bottom	78	86	1050	117	110

^{1/} All samples taken from ingot interior.^{2/} Analyses not obtained.

patterns for the ingot in figures 18 and 19 is shown in figure 21. This figure shows hardness values on the plane through the center of the ingot and parallel to the 20-inch axis of the cross section. The increased hardness noted along the lower part of the ingot is attributed to impurities in the slag. During melting of this ingot, all of the slag was added to the crucible prior to the start of melting, and the first titanium melted gettered the slag and caused an increase in impurity content at the bottom of the ingot.

Good quality ingots were prepared by electroslog melting in a 12-inch-diameter round crucible. Figure 22 is a photograph of an ingot prepared by melting vacuum-distilled sponge in calcium fluoride slag. Some roughness of the sidewalls of this ingot is evident; however, for the most part, the sidewalls were considered satisfactory for forging with only a minimum of machining. Data obtained during melting of this ingot (SA 26, 475) and a similar ingot (SA 26, 457) prepared from a domestic sponge are included in table 8. This second ingot is shown in figure 23.

While the ingot prepared from domestic sponge did not have smooth sidewalls, the internal structure was sound. The sidewalls on the upper half of the ingot were much rougher than on the lower half, presumably as a result of depletion of the slag cover during melting. As in all other runs in the prototype furnace, the entire charge of slag was placed in the crucible at the start

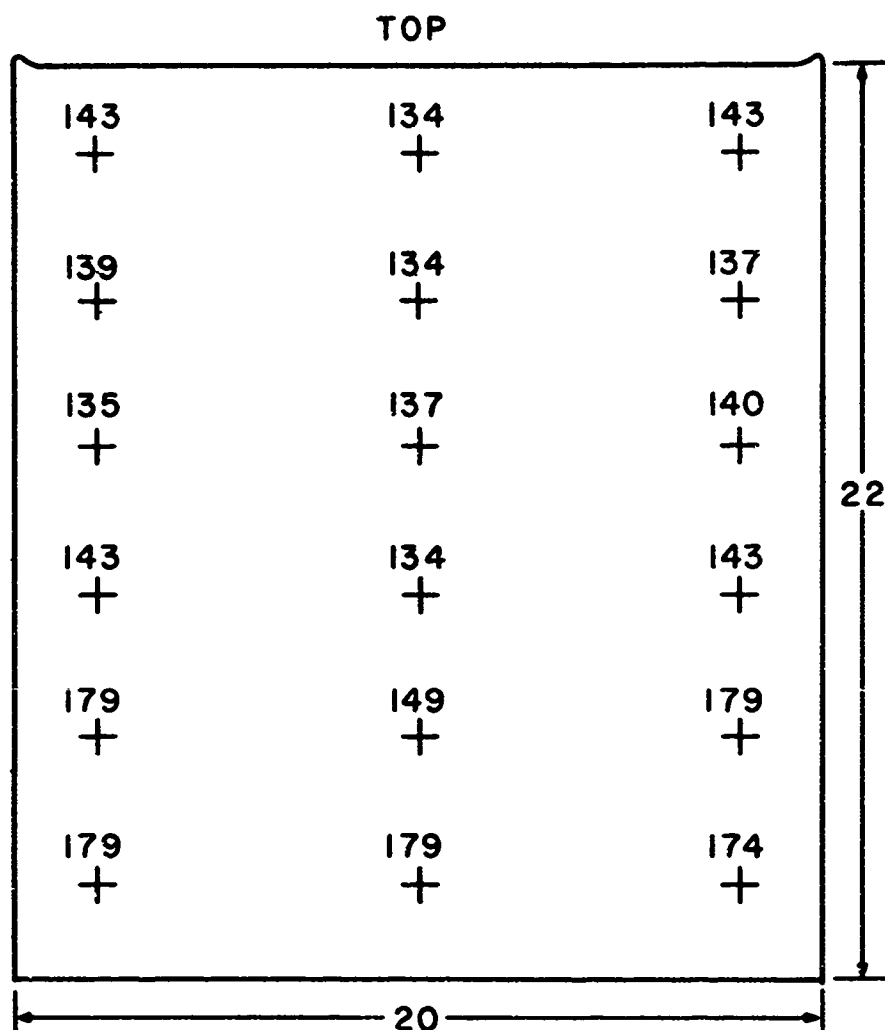
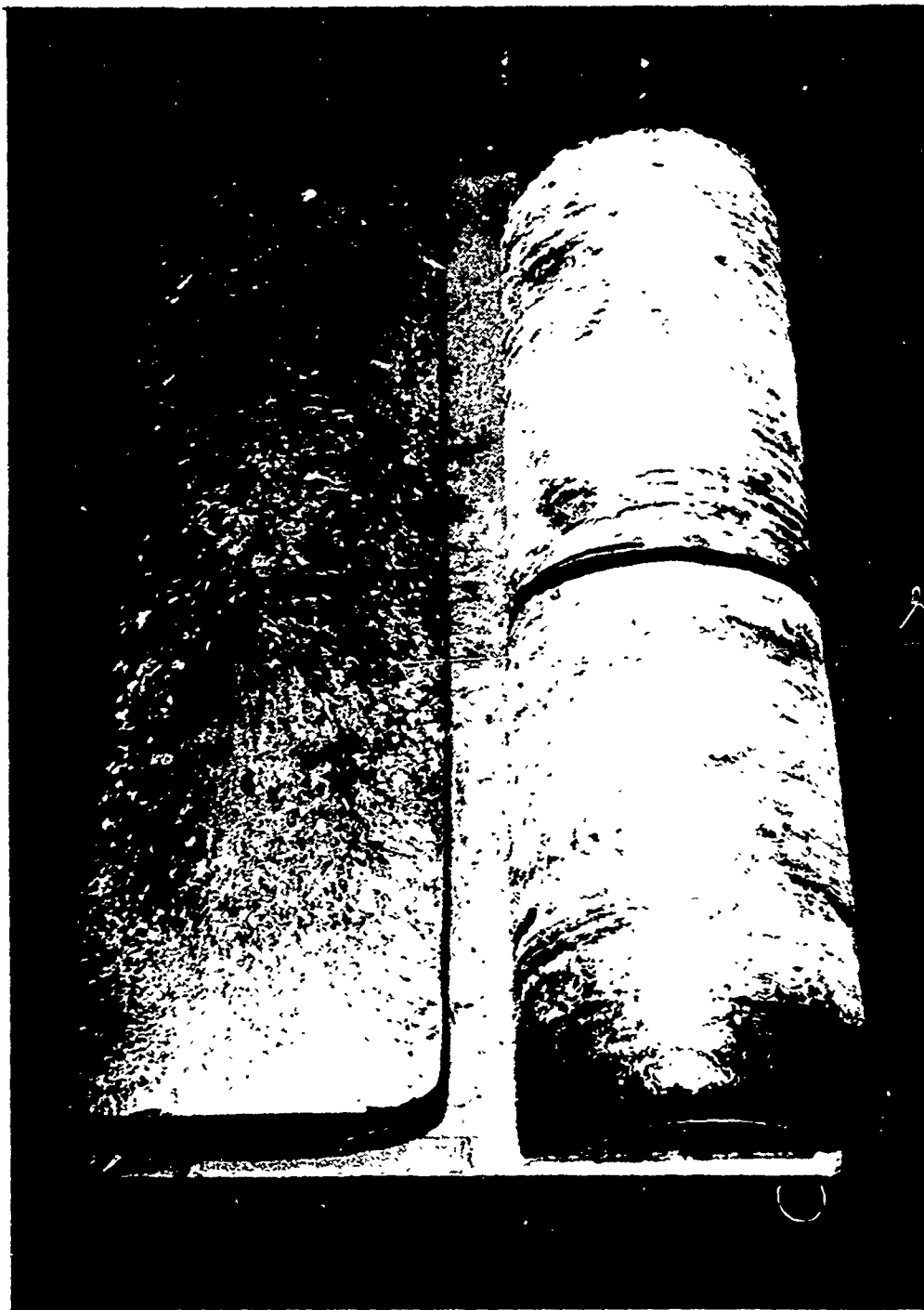


FIGURE 21.-Variation in Brinnell Hardness
as Measured on the Interior Surface of
Electroslag-Melted Ingot SA25,835
(leached and dried sponge).

68-277



FIGURE 22. - Electroslog-melted, 12-inch-Diameter Ingot of Vacuum-distilled Titanium Sponge



**FIGURE 23. - Electroslog-melted, 12-inch-diameter Ingot of Gas-sweep
Processed Titanium Sponge**

of the run. The run was sufficiently unstable to cause frequent eruptions of the slag pool with a considerable resultant loss of slag from the crucible. It is also possible that the slag became sufficiently contaminated with chlorides by the time the run was half finished to cause the sidewall roughness noted. No differences in furnace operation were noted which could explain the marked difference between the upper and lower ingot halves. A similar change in ingot sidewall quality as a function of ingot length was not observed during melting of slab-shaped ingots.

The following recommendations for industrial use are made as a result of experience gained with the prototype furnace:

1. Large-scale round ingots, suitable for direct fabrication, can be prepared from vacuum-distilled titanium sponge by electroslag melting in purified calcium fluoride. A liquid slag starting procedure would be superior to starting with a solid slag, but ingots can be prepared by the methods used in this work. Ingots prepared from domestic sponge containing large amounts of volatiles will not be satisfactory for direct conversion to plate and sheet.

2. Power requirements for electroslag melting are greater than for vacuum arc melting. An arc current slightly in excess of 1,000 amperes per inch of ingot diameter serves as a guide in determining requirements for electroslag melting. For example, a 4-inch-diameter ingot requires approximately 4,500 amperes of melting current at 24 volts potential; a 6-inch-diameter

ingot was melted with excellent results at a melting current of 6,500 to 6,800 amperes at 22 to 24 volts potential. The best 12-inch-diameter ingot was melted at 13,000 to 13,500 amperes at 27 to 28 volts potential; however, the melting rate for this run was very low, and better results might have been obtained at a higher power input.

3. Slightly better slab-shaped ingots were obtained with electrodes of smaller cross section. The results obtained were not clearly defined, however, because the improvement obtained was relatively minor. Similar studies with large-scale round ingots were not conducted.

4. Slag used for electroslag melting of titanium must be carefully pretreated prior to use. Sufficient slag must be maintained in the crucible to allow melting at up to 30 volts potential. When the slag depth is too shallow, the electrode cannot be submerged in the slag without reducing the melting potential to such a low value that the melting rate is very low. The 6-inch ingot was melted with a minimum slag depth of 1-1/2 inches, and sufficient slag was maintained in the large-scale runs for at least 3 inches of slag.

THE SLAG

Available Materials

Titanium melting places great restrictions on possible slag compositions suitable for study. Oxide components are of no use since titanium can react with many of the oxides found in steelmaking slags to form stable titanium oxide. (For example, the standard free energies of formation of TiO_2 , Ti_3O_5 , and Ti_2O_3 at $2,000^\circ \text{K}$ are -140 , -382 , and -237 kcal, respectively.) In general, borides, carbides, and nitrides melt at temperatures too high for practical use ($2,200$ to $3,900^\circ \text{C}$), or decompose at $<1,000^\circ \text{C}$, and therefore the halides are the most suitable anionic materials. Alkali metal halides invariably possess unsuitably high vapor pressures. (The boiling points all range from approximately $1,200^\circ$ to $1,700^\circ \text{C}$.)

High vapor pressures and reactivities due to unfilled inner shells of the metals are also characteristic of most of the transition metal halides, and their variable valency permits easy undesirable halide transfer at temperatures of interest. Another factor to be considered is that titanium acts as an excellent getter for a number of elemental impurities such as Al, Fe, Si, and O which occur in the more common slag compositions. It therefore appears that the alkaline-earth and lanthanon (rare earth + yttrium) halides offer the best prospects as slag compositions for the electroslag melting of titanium. Slags composed entirely of alkaline-earth and lanthanon chlorides, bromides, and iodides,

however, are also unsuitable due to the relatively high vapor pressures of these components at temperatures of interest and consequent low boiling temperatures. However, Russian workers (8) have stated that in practice a titanium welding flux "containing fluorides only, does not possess the required technological qualities" and that some of the fluorides should be replaced by chlorides. In general the chlorides possess lower melting and boiling points than fluorides, and it is therefore possible that suitable chlorides with higher vapor pressures would act as sweeping agents to remove or reduce some gaseous impurities from the molten metal at temperatures of interest. Pertinent properties of the more suitable alkaline-earth and lanthanon fluorides as well as CaCl_2 are summarized in table 9.

Further considerations which must influence the choice of slag composition for titanium melting include the overall stability of the slag at temperatures of interest. This requires a knowledge of the thermodynamic properties (for example, high temperature heat contents, heats of formation, free-energies of formation and activities) of the components in the molten slag bath. A good slag must possess sufficient stability with respect to the metal so that it does not contribute harmful impurities to the latter phase, and it is preferable to choose a slag with a low vapor pressure at high temperatures.

Thermodynamic calculations (table 10) indicate that titanium is not likely to react with the fluorides listed in table 9 or CaCl_2 at a temperature believed to be close to that which obtains during the melt ($\sim 2,000^\circ \text{K}$). However, free

TABLE 9. - Properties of alkaline-earth and lanthanon fluorides suitable for electroslag melting of titanium (CaCl₂ included for comparison.)

Composition	Melting point, °C	Boiling point, °C (one atm.)	Vapor pressure at 2,000° K (log atm.)	ΔG° at 2,000° K (kcal)	ΔH _{fusion} (cal. mole ⁻¹)	Density 1/		Crystal structure
						298° K	2,000° K	
MgF ₂	1,263 (24) ^{2/}	2,227 (24)	-1.66 (12)	-172. (7)	13,900 (24)	3.14 (20)	2.19 (11)	Tetragonal (22)
CaF ₂	1,418 (24)	~2,500 (22)	-2.41 (12)	-210. (7)	6,780 (24)	3.20 (20)	2.40 (11)	(Rutile) Cubic (22)
SrF ₂	1,486 (23)	2,477 (24)	-2.27 (12)	-210. (7)	4,260 (24)	4.24 (22)	3.28 (11)	(Fluorite) Cubic (22)
BaF ₂	1,320 (24)	2,200 (24)	-1.61 (12)	-214. (7)	3,000 (24)	4.91 (20)	3.78 (11)	(Fluorite) Cubic (22)
YF ₃	1,152 (6)	2,227 (6)	No data	-300. (7)	13,000 (6)	5.07 (6)	No data	(Fluorite) Orthorhombic (6)
LaF ₃	1,493 (6)	2,327 (6)	-2.40 (6)	-315. (7)	8,000 (6)	5.94 (6)	4.43 (11)	Cubic Hexagonal (6)
CaCl ₂	782 (24)	~2,000 (24)	No data	-128. (7)	6,780 (24)	2.15 (22)	No data	Close packed Cubic (22) (Fluorite)

1/ For comparison, the density of molten titanium at 2,000° K, calculated from a formula given by Maurakh (16), is 4.08 gm. cm⁻³.

2/ Numbers in parentheses refer to references at the end of this report.

TABLE 10.- Standard free energies of reaction at 2,000° K

Reaction	Calculated ΔG° (kcal) at 2,000° K		
	<u>n = 2</u>	<u>n = 3</u>	<u>n = 4</u>
$\frac{n}{2} \text{MgF}_2 + \text{Ti} = \text{TiF}_n + \frac{n}{2} \text{Mg}$	+ 11.	+ 16.	+ 43.
$\frac{n}{2} \text{CaF}_2 + \text{Ti} = \text{TiF}_n + \frac{n}{2} \text{Ca}$	+ 46.	+ 68.	+ 113.
$\frac{n}{2} \text{SrF}_2 + \text{Ti} = \text{TiF}_n + \frac{n}{2} \text{Sr}$	+ 42.	+ 62.	+ 105.
$\frac{n}{2} \text{BaF}_2 + \text{Ti} = \text{TiF}_n + \frac{n}{2} \text{Ba}$	+ 54.	+ 80.	+ 129.
$\frac{n}{3} \text{YF}_3 + \text{Ti} = \text{TiF}_n + \frac{n}{3} \text{Y}$	+ 17.	+ 24.	+ 55.
$\frac{n}{3} \text{LaF}_3 + \text{Ti} = \text{TiF}_n + \frac{n}{3} \text{La}$	+ 36.	+ 35.	+ 69.
$\frac{n}{2} \text{CaCl}_2 + \text{Ti} = \text{TiCl}_n + \frac{n}{2} \text{Ca}$	+ 56.	+ 96.	+ 128.

Data obtained from references (21) for MgF_2 and TiF_n ,
 (7) for CaCl_2 and TiCl_n , and (24) for all others.

alkaline-earth elements and titanium fluorides or subfluorides are possible reaction products if phenomena other than thermochemical processes predominate. Such phenomena include electrolysis, effects of physicochemical properties, nonequilibrium effects, solubilities, and mechanical and electrical parameters during melting. These effects must be taken into account when utilizing thermochemical calculations for predictions of what actually occurs during melting.

Additional factors which must be considered are (1) the heat of fusion must be low enough so that the slag can be relatively easily melted; (2) the slag melting point must be close to but slightly less than that of the metal; (3) the electrical conductivity should be less than that of the metal yet high enough to facilitate initiation of melting as well as to stabilize the melting operation, and (4) the thermal conductivity should be as low as possible to provide an insulating cap on the ingot, thus reducing the thermal gradient at the top of the ingot during and after melting. Thermal capacity and surface tension must also be taken into consideration.

It is desirable to work with a slag with a sufficiently high fluidity at operating temperatures, with one which will remove unwanted impurities (which might form inclusions) and one which will improve the metal structure as well as protect the metal from the ambient atmosphere and prevent reactions with the crucible. In general, the slag should be capable of establishing and steadily maintaining the melting process and exerting a cleansing action as well as eliminating cold shuts and rough ingot surfaces.

Unfortunately, sufficient data to evaluate quantitatively the physicochemical parameters such as viscosities, densities, thermal-, and electrical conductivities of molten slags are not available. Data such as these would be extremely useful especially in evaluating optimum operating conditions as a function of slag composition. In addition, considerable research to establish basic thermodynamic properties is needed for an accurate prediction of chemical processes which occur during electroslag melting. However, a small amount of thermochemical data is available to permit a semiquantitative evaluation of optimum slag compositions for use in titanium melting. Consider a reaction involving a suitable fluoride slag with hydrogen, which is one detrimental impurity in titanium melting. Values for the standard free-energies of reaction at 2,000° K are given below from reference (7):

<u>Reaction</u>	<u>ΔG° (kcal) at 2,000° K</u>
$\text{MgF}_2 + \text{H}_2 = 2 \text{ HF} + \text{Mg}$	+ 38.
$\text{CaF}_2 + \text{H}_2 = 2 \text{ HF} + \text{Ca}$	+ 78.
$\text{SrF}_2 + \text{H}_2 = 2 \text{ HF} + \text{Sr}$	+ 78.
$\text{BaF}_2 + \text{H}_2 = 2 \text{ HF} + \text{Ba}$	+ 80.
$2/3 \text{ LaF}_3 + \text{H}_2 = 2 \text{ HF} + 2/3 \text{ La}$	+ 78.
$2/3 \text{ YF}_3 + \text{H}_2 = 2 \text{ HF} + 2/3 \text{ Y}$	+ 74.

The value for MgF_2 is considerably less positive than the others, which means there is a greater chance that this slag composition will actively remove hydrogen from the titanium metal during a run at $2,000^\circ \text{K}$. Therefore, pure MgF_2 was chosen as one of the slag compositions to be studied. It is also possible that suitable mixtures of MgF_2 in CaF_2 may produce a still more favorable composition in terms of removing hydrogen from the metal, especially if the liquid solutions in this system exhibit positive deviations from Raoult's Law.

It is also possible that oxygen and/or hydrogen may be removed from titanium during electroslag melting by means of additions of small amounts of another more electropositive metal to the slag. Significant solid solubility of the metal in titanium should be avoided to preclude additional contamination during ingot solidification. The metal should also be capable of forming more stable oxides and/or hydrogen compounds. The oxygen and/or hydrogen for formation of such compounds would presumably be derived from the impurities in the titanium metal. An examination of the available phase equilibrium data involving binary metal systems (5, 10) indicates that nearly all metals are soluble in solid titanium to a certain degree. Exceptions to this are yttrium, thorium, and boron. Yttrium is slightly soluble in titanium (0.5 atomic percent Y at $1,360^\circ \text{C}$ in β -Ti and approximately 0.05 atomic percent Y at 875°C in α -Ti (5).) Thorium shows no solid solubility with titanium and forms a eutectic system. The same is true for boron except that several intermediate compounds are formed. Lanthanum would be another possible slag additive inasmuch as

it is believed that no compounds are formed in the possible eutectic system with titanium (10), and possibly there exists a miscibility gap in the liquid state which would indicate negligible solid solution. Magnesium may be still another alternative.

On the basis of thermochemical calculations at 2,000° K, similar to those given previously for the alkaline-earth fluorides and titanium, it can be shown that yttrium, lanthanum, and thorium could react with a number of titanium oxide phases to form the respective oxides. This is not the case with boron, and the reaction is only favorable with TiO_2 in the case of magnesium.

For a reliable estimate of the desired optimum composition (of fluoride systems as well as metal-fluoride systems) knowledge of the activities of the two components in the liquid solution at high temperatures is essential in order to evaluate the appropriate free-energies. As far as is known, no direct experimental high-temperature thermochemical data are available, and thus estimates of the high-temperature activities must be made. This is most conveniently accomplished by the use of the phase equilibrium data and the following equation presented by Kubaschewski, Evans, and Aicock (12) for systems in which no significant solid solubility is observed, as is the case for $\text{MgF}_2\text{-CaF}_2$,

$$\log a_{\text{CaF}_2} = - \frac{(T_{\text{CaF}_2} - T_c) L_{\text{CaF}_2}}{4.574T \cdot T_{\text{CaF}_2}} + \frac{T - T_c}{T} \log N_{\text{CaF}_2} \quad (1)$$

Here, T represents an arbitrary absolute temperature ($^{\circ}\text{K}$) at which the activities are to be calculated; L_{CaF_2} denotes the heat of fusion of CaF_2 at its melting point T_{CaF_2} ; N_{CaF_2} is the mole fraction of CaF_2 ; and T_c is the liquidus temperature at this composition. The activity of MgF_2 in the liquid solution can then be obtained using the results from equation (1) and a Gibbs-Duhem integration. The results are only an estimation inasmuch as the liquid solution is assumed to be regular. This means that there is no entropy change involved in the transfer of a constituent from a regular solution to an ideal solution of the same concentration, the exchangeable cations occupy random sites as in an ideal solution, and the heat of mixing is not zero. The molar heats are assumed to be additive. Of course the heat of fusion for CaF_2 should be known accurately, and it is preferable to know the liquidus curve within $\pm 0.2^{\circ}$, which is usually not the case. The above derivation also neglects the heat capacity changes on melting. Nevertheless, this method provides a useful approximate means for evaluating activities when direct experimental data are unavailable, and hence a rough estimate of suitable compositions within the system can be determined.

Slag compositions of reagent- and acid-grade CaF_2 , MgF_2 , two mixtures involving approximately 4 and 12 weight-percent MgF_2 in CaF_2 , SrF_2 - CaF_2 , LaF_3 - CaF_2 mixtures, LaF_3 , a MgF_2 - CaF_2 - LaF_3 mixture, CaCl_2 - CaF_2 mixtures, and Y - CaF_2 mixtures were selected for study, primarily based on factors enumerated above.

Need for and Schemes for Treatment

Morozov and coworkers (17) have demonstrated that ingots produced with untreated CaF_2 slag are unsatisfactory with respect to impurities and mechanical properties. Although impurity contents vary according to lot, Al, Cr, Fe, Mg, and Si are present ranging from 30 parts per million (ppm) up to 3 percent in as-received CaF_2 and MgF_2 . A few ppm of Mg and Si were the only impurities observed in untreated LaF_3 . In addition, approximately 0.15 percent C, and 0.11 and 0.59 percent CO_2 were present in as-received reagent- and acid-grade CaF_2 , respectively. It was also noted that the as-received CaF_2 and CaCl_2 contained considerable moisture. Therefore it is evident that some method of heat treatment is required before the slag can be used in titanium melting.

An evaluation was conducted of various methods of treatment by means of equipment available in this laboratory. In all cases, after having been isostatically pressed and crushed, the untreated slag was heated for approximately two hours at 600° to 650° C in air in a muffle furnace, primarily to eliminate moisture and any other relatively volatile impurities. However, this initial treatment did not substantially decrease the impurities present in the untreated material. Upon heating, Al and Fe decreased slightly in reagent-grade CaF_2 , Si was lowered in acid-grade CaF_2 , and Ca and Fe were slightly lower in MgF_2 . All other impurities showed no change or actually increased as a result of this heating.

At this stage of treatment, presumably little or no CO_2 had been removed and the level of impurities was still higher than desired. Therefore, all slags were fused in either a graphite resistor furnace or a melting furnace utilizing a nonconsumable titanium electrode in a water-cooled copper crucible. The pressed, heated, and crushed slag should be fused with minimum delay in order to minimize absorption of moisture. Noticeable evolution of HF and other volatiles is evident during fusion of a slag which has been stored for any period of time. A sulfide odor sometimes noted during the subsequent fusion was probably due to the sulfate material remaining from the as-received material.

The resistor furnace ^{6/} allowed approximately 3.5 kg of material to be fused at a time when a liner was used inside the large graphite container. The melting furnace accepted twice this amount for one run. Fusions in the resistor furnace were conducted with and without a TZM (Mo-0.5 wt pct Ti-0.08 wt pct Zr-0.015 wt pct C) liner and titanium chips. It was thought that the latter might act as an impurity getter at temperatures used in the slag-fusion process. It is important for minimum fused slag discoloration that even no minor leaks be present in the furnace. Analytical results on the fused products employing the various techniques mentioned above are enumerated in table 11. Examination of this table shows that the Al, CO_2 , and Si impurity concentrations appear to be independent of the type of fusion treatment and the slag composition used.

^{6/} This furnace is described in detail in Lustman and Kerze (14).

TABLE 11-- Impurities in fused unused slags

Fusion technique	Slag composition	Al	C	Ca	CO ₂	Cu	Fe	Mg	Mn	Mo	N	Ni	Si	Ti	Y	Zr
Melting furnace	Reag. CaF ₂	D+	.0213	A+	.05	---	E+	---	---	---	---	---	C	1.44	D+	---
	do.	.032	.0087	A+	.013	E+	.007	.105	---	---	.0019	---	<.021	<.05	D+	---
	do.	.082	.0149				.016	.09			.0044		.021			
	Acid CaF ₂	.031	.0432	A+	.015	F	.002	<.01	---	---	.0026	---	.15	1.87	---	---
Resistor furnace; (No liner, no Ti)	Reag. CaF ₂	1/.012	.0266	A+	.005	---	.012	.10	---	D	.0026	C	.041	.08	E+	---
	12 wt pct MgF ₂ in CaF ₂	.019	.0074	A+	.01	---	.008	3.00	---	D+	<.0010	---	.047	.07	D+	D
Resistor furnace; (No liner, Ti)	Reag. CaF ₂	2/.017	.0448	A+	.01	---	.013	---	---	---	.0020	---	.038	.096	---	---
	do.	.046	.0663	A+	.01	---	.010	---	---	---	.0015	---	.040	.032	---	---
	do.	C	.0922	A+	.03	---	E+	---	---	---	---	---	C	.066	---	---
	do.	C	.0303	A+	.02	---	E+	---	---	---	---	---	C	.32	---	---
	do.	1/.041	.0907	A+	.014	---	.026	.10	---	D		D	.063	.10	E+	---
	do.	3/.061	.0526				.005	.009			.0032		.052			
	do.	.048	.0420	A+			.015	.12	---	D	.0021	---	.044	1.33	---	---
	MgF ₂	4/E+	.0111	C	.023	E+	D	A+	D	---	---	---	D+	.38	---	---

(Continued)

TABLE 11. - Impurities in fused unused slags (Continued)

Fusion technique	Slag composition	Al	C	Ca	CO ₂	Cu	Fe	Mg	Mn	Mo	N	Ni	Si	Ti	Y	Zr
Resistor furnace;	Reag. CaF ₂	D+	.0037	A+	---	---	---	F+	---	E+	.0015	---	E+	D+	---	---
(TZM liner, 4 wt pct MgF ₂ no Ti)	do.	D+	.0023	A+	---	---	---	F	---	D	.0020	---	E+	D+	---	---
	in CaF ₂	.008	.0029	A+	.03	---	.011	1.87	---	C	<.0010	---	.062	.03	---	---
	52 wt pct LaF ₃															
	in CaF ₂	.063	.0167		.028		.070	.06			.0041		<.005	.16		
	18.5 wt pct SrF ₂															
	in CaF ₂	.032	.0109				.022	.04			.0023		.064			
Resistor furnace;	LaF ₃	.018	.0025	---	.04	---	.022	<.01	---	---	---	---	---	C	---	---
(Mo liner, no Ti)																
Resistor furnace;	Reag. CaF ₂	.014	.0200	A+	.072	---	.003	.13	---	C	.0017	---	.076	B	---	D
(TZM liner, MgF ₂ Ti)	Acid CaF ₂	.035	.0076	A+	.05	---	.016	.22	E	B	<.0010	---	.18	C+	---	---
		.005	.0123	.34	.01	---	.006	A+	---	D+	.0011	---	.039	.17	---	---

1/ Cr content for this slag is C; Cr not detected spectrographically in all other slags listed above.	A+ = 10-100%	C = 0.03-0.3%	E+ = 0.001-0.01%
2/ Oxygen content for this slag is 0.09%.	B = 0.3-3%	D+ = 0.01-0.1%	E = 0.0003-0.003%
3/ Cl content for this slag is 0.044%.	C+ = 0.1-1%	D = 0.003-0.03%	F+ = 0.0001 -
4/ Oxygen content for this slag is 0.077%.			F = 0.001%
			F = 0.00003 -
			0.0003%

All numerical values reported in percent impurity.

--- Not detected spectrographically.

The same is true for Fe except when reagent-grade CaF_2 is fused in the resistor furnace with a liner and no Ti. In this case Fe is reduced in the slag. Carbon contents are generally lower in slags fused in the melting furnace and in the resistor furnace with TZM liner and no Ti and appear to be highest in slags melted in the resistor furnace without a liner and with titanium. If titanium is not present, there appears to be little difference in slag carbon content from that fused in a TZM liner. All fusion methods reduce both the C and CO_2 contents from the as-received material. It is apparent from the table that the addition of titanium chips does not effectively getter impurities from the slag, presumably because the titanium is not molten at the temperatures used in fusing the slag. In some cases the slag impurity content increases when titanium is added, therefore it is recommended that an inert liner be used, primarily to minimize carbon pickup, and that no titanium chips be included in the fusion step. In this case, the magnesium content of CaF_2 slags is also lower. Acid-grade CaF_2 slags fused in the melting furnace were found to contain traces of titanium suboxides and calcium silicates.

A substantial economic advantage is realized if acid-grade CaF_2 (6¢ to 75¢/lb) can be effectively substituted for the reagent-grade material (\$2.00 to \$5.00/lb). The impurity contents of these two slags from the as-received material through the fusion step are compared in table 12 where the CO_2 contents provide a measure of the CaCO_3 present in both slags. These data also show

TABLE 12.- Comparison of impurity content in acid-grade and reagent-grade calcium fluoride. (All values in parts per million.)

Impurity	Acid-grade		Reagent-grade	
	As-received	650° C heating	As-received	650° C heating
				2/ Average fused
Al	300-3,000	300-3,000	300-3,000	100-1,000
C	1,580		1,500	
CO ₂	5,920		1,050	
Cr	3/ ---	---	30-300	---
Fe	30-300	30-300	30-3,000	10-100
Mg	10-100	10-100	300-30,000	3,000-30,000
N				
Si	3,000-30,000	1,000-10,000	300-3,000	300-3,000
Ti	---	10-100	---	300-3,000
				<3,904

1/ Average of 2 lots.

2/ Average of 6 lots.

3/ --- Not detected spectrographically.

that acid- and reagent-grade CaF_2 slags are comparable in impurity contents, and that MgF_2 slags show the same trends as reagent-grade CaF_2 . The relative effectiveness of these slags in removing impurities will be discussed later.

X-ray diffraction measurements generally show a certain amount of ionic substitution of an unknown species in the CaF_2 lattice after fusion and in the used CaF_2 slag. The latter also includes traces of unknown nonmetallic phases. No substitution is evident in the as-received CaF_2 and MgF_2 material. Used LaF_3 - CaF_2 contains an expanded CaF_2 lattice, indicating solid solution of LaF_3 , inasmuch as the ionic radius of La^{3+} is larger than that of Ca^{2+} . Also present are traces of LaF_3 and an unknown phase. Used CaCl_2 - CaF_2 slag shows primarily CaF_2 with traces of a CaFCl compound and TiF_3 . Optical studies on reagent-grade CaF_2 fused in the melting furnace show primarily the fluoride with numerous inclusions, and well distributed titanium metal together with a small amount of a further nonmetallic phase. Material fused in the resistor furnace shows less metal which tends to concentrate at the CaF_2 grain boundaries. Used reagent-grade CaF_2 shows little change from the unused fused material except that the well-distributed metal phase is more concentrated in the sidewall slag, and a tendency toward grain boundary concentration was noted in the top slag. Used MgF_2 contains a uniformly distributed metal phase, and the unused MgF_2 - CaF_2 slags show two exsolved phases as predicted by the phase diagram. Unused fused LaF_3 - CaF_2 slag shows a single nonbirefringent phase and minor

amounts of at least one other phase. This is also true for the used slag, which also contains a well dispersed metallic phase and an additional birefringent phase.

In order to ascertain the distribution of impurities throughout the slag billet and therefore to evaluate sampling procedures, analyses for different areas within unused and used slag billets were performed. These results, together with calculated standard deviations and standard errors, which reflect the internal consistency of the samples, are given in table 13. Table 13 A, demonstrates that grab sampling a 6.8 kg fused CaF_2 billet is inadequate for analytical work. A preferred sampling procedure is to first crush the material and subsequently obtain a split sample before grinding. The impurity variation is nearly as great in used CaF_2 top slag weighing 0.90 kg, as shown in table 13 B.

Another problem which has a bearing on slag economics is the degree to which a slag can be reused without further treatment. Data pertinent to this question concerning CaF_2 slags are shown in table 14. In general, the sidewall slag becomes increasingly more contaminated and is therefore not suitable for reuse. On the other hand, the top slag impurity content remains at an approximately constant level so that reuse is possible, particularly if one considers the inertness of this slag for actively absorbing impurities during melting. This point will be considered more fully later. Note particularly the lack of Mg buildup in the reused slag. Repeated slag use, however, is likely to increase electrical power outlay due to increasing electrical conductivity as a result of changes in slag chemistry, and thereby decrease productivity.

TABLE 13- Distribution of impurities in CaF₂ slag billetsA. Melting furnace fused CaF₂ billet:

	Impurity						
	Al	C	CO ₂	Fe	Mg	Si	Ti
(1)	0.068	0.0191	0.005	0.014	0.08	0.039	<0.03
(2)	0.013	0.0128	0.012	0.003	0.07	0.004	0.07
(3)	0.010	0.0049	0.008	0.001	0.10	0.033	0.16
(4)	0.012	0.0084	0.006	0.005	0.09	<0.004	0.07
Mean	0.026	0.0113	0.008	0.006	0.085	<0.020	
$\pm \sigma$	± 0.024	± 0.0053	± 0.003	± 0.002	± 0.01	± 0.016	
Standard error	0.014	0.0030	0.002	0.001	0.006	0.009	

(1) Collar slag

(2) Center - bottom of billet in contact with base plate

(3) Center - middle of billet

(4) Center - top of billet

B. Used CaF₂ top slag billet from a small-scale run:

	Impurity					
	Al	C	Fe	Mg	N	Si
(5)	0.015	0.0107	0.004	0.13	0.0040	<0.002
(6)	0.025	0.0113	0.002	0.10	0.0011	<0.002
(7)	0.026	0.0117	0.001	0.07	0.0016	0.002
(8)	0.065	0.0133	0.001	0.13	0.0011	<0.002
Mean	0.033	0.0118	0.002	0.11	0.0020	
$\pm \sigma$	± 0.019	± 0.0010	± 0.001	± 0.02	± 0.0012	
Standard error	0.011	0.0006	0.001	0.01	0.0007	

All values reported in percent impurity.

(5) Center of top slag in contact with ingot

(6) Outside edge of top slag - top 1/2 inch

(7) Outside edge of top slag - bottom 1/2 inch

(8) Sidewall slag

TABLE 14.- Analytical data for reagent-grade CaF₂

<u>Impurity</u>	<u>Fused slag</u>	<u>Used slag</u>		<u>Reused slag</u>	
		<u>Top</u>	<u>Sidewall</u>	<u>Top</u>	<u>Sidewall</u>
Al	D+	0.017	0.024	0.019	0.059
C		0.0055	0.0082	0.0028	0.0185
CO ₂	0.033	0.01	0.02	0.04	0.01
Cu	---	---	E	E	E
Fe	E+	<0.001	0.006	0.002	0.002
Mg	B	0.05	0.21	0.05	0.11
Mo	D	D+	E+	D	B+
Si	C	0.014	0.009	0.006	<0.002
Ti	A	0.20	0.07	0.10	0.10

All values reported in percent impurity are from wet chemistry and values reported by letters are from spectrographic determinations as follows:

A = 3-30%
 B+ = 1-10%
 B = 0.3-3%
 C = 0.03-0.3%
 D+ = 0.01-0.1%
 D = 0.003-0.03%
 E+ = 0.001-0.01%
 E = 0.0003-0.003%

--- Not detected spectrographically.

Attempts to measure the surface temperature of the molten slag bath during the melt by a two-color (ratio) pyrometer have met with limited success. For most of the slag compositions studied, the operating conditions are sufficiently erratic to cause a wide variation in radiation intensity during the run. Use of the two-color or ratio pyrometer minimizes the effect of vapor and particulate matter present over the slag bath. Accurate temperature measurements with this instrument are dependent upon the relative independence of the slag emissivity with wavelength. Thus, the advantages of this pyrometer over the conventional optical pyrometer (which was used to monitor temperatures during the slag fusion step where fewer vapors and more quiet conditions are obtained) are obvious.

Integrated temperature measurements over a specified time interval indicate that when reagent-grade CaF_2 is used, the top of the slag bath is $1,680^\circ \pm 40^\circ \text{C}$. When varying amounts of CaCl_2 are added to CaF_2 , this temperature decreases somewhat. Additions of LaF_3 , and/or MgF_2 to the slag render conditions too erratic for meaningful temperature measurements by this method.

Partition of Slag and Sponge Impurities

For titanium melted under a variety of slag compositions and recycled slags, selected impurity analyses in unused and used slags and electrode metal and final ingot are shown in table 15. The unused slag analyses represent those

TABLE 15. - Impurity concentrations (ppm) in metal and slag phases before and after titanium electroslag melting

Run	Slag	Impurities (Fluorine and chlorine analyses given in footnotes)									
		Al	C	CO ₂	H	Fe	Mg	N	O	Si	Ti
SA 25, 897 1/	Reag. CaF ₂ 7/	610	526	Unused slag		50	90	32		520	
	No liner	680	89	Used slag		150	1100	56		<70	
	Ti	<50	92	Electrode	20	375	250	34	705	100	
	Ingot 5/	<75	135	Ingot 5/	16	400	80	72	872	225	
SA 26, 253 1/	Reag. CaF ₂ 8/	660	111	Unused slag		160	800	350		220	
	Used slag	445	207	Used slag		190	3100	52		205	
	Electrode	<50		Electrode		300	150			<100	
	Ingot 6/	<50	97	Ingot 6/	45	433	52	132	674	<100	
SA 26, 061 1/	Reag. CaF ₂ 7/	170	448	Unused slag		130	---	20	900	380	960
	No liner	300	469	Used slag		40	<350	22	1400	40	2000
	Ti	<50	32	Electrode	18	750	<15	107	800	150	
	Ingot 5/	<50	135	Ingot 5/	23	400	23	70	901	250	
SA 26, 249 1/	Reag. CaF ₂ 7/	350	69	Unused slag		200	900	13		50	
	with TZM liner	640	110	Used slag		<10	1700	<14		<20	
	No Ti	<50	92	Electrode	20	375	250	34	705	100	
	Recycled top slags	50	104	Ingot 5/	23	300	55	47	828	150	
SA 26, 077 1/	Reag. CaF ₂ 7/	480	420	Unused slag		150	1200	21		440	13,300
	No liner	700	3275	Used slag			4500	33		90	2000
	lined crucible	<50	92	Electrode	20	375	250	34	705	100	
	used	83	564	Ingot 5/	20	317	60	98	665	200	

(Continued)

TABLE 15.- Impurity concentrations (ppm) in metal and slag phases before and after titanium electroslag melting (Continued)

Run	Slag	Impurities (Fluorine and chlorine analyses given in footnotes)									
		Al	C	CO ₂	H	Fe	Mg	N	O	Si	Ti
SA 26, 084 1/ Air melt	Reag. CaF ₂ 7/	460	663	100		100		15		400	320
	No liner	650	87			<10	2100	610		70	
	Ti	<50	92		20	375	250	34	705	100	
	Electrode	<50	92		19	300	35	1638	2235	100	
SA 26, 158 2/ With TZM liner	Reag. CaF ₂ 7/	140	200	720		30	1300	17		760	
	Used slag	550	158	420		15	7900	<19		50	
	Ti	450	64		66	425	4000	125	580	150	
	Electrode	200	94		172	575	50	127	586	200	
SA 26, 159 2/ No liner	Reag. CaF ₂ 7/	120	266	50		120	1000	26		410	800
	Used slag	140	82	310		45	8700	<15		<35	1000
	No Ti	450	64		66	425	4000	125	580	150	
	Electrode	200	56		194	575	65	119	705	200	
SA 25, 835 2/ Reag. CaF ₂ 8/	Unused slag	700	380	100		110	1700	<10		340	
	Used slag		66	<500			5300	<10			
	Electrode	200	124		122	400		45	702	<100	
	Ingot 6/	500	113		189	667	93	63	784	283	
SA 25, 934 3/ Reag. CaF ₂ 8/	Unused slag	720	820	340		180	1900	277		480	
	Used slag	610	39	510		---	2600	<15		50	
	Electrode	<50	178		18	500	400	50	500	<100	
	Ingot 6/	117	77		79	800	150	108	787	<100	

(Continued)

TABLE 15.- Impurity concentrations (ppm) in metal and slag phases before and after titanium electroslag melting (Continued)

Run	Slag	Impurities (Fluorine and chlorine analyses given in footnotes)									
		Al	C	CO ₂	H	Fe	Mg	N	O	Si	Ti
SA 26, 157 4/	Reag. CaF ₂ 8/	Unused slag	380	87	130	70	1050	19		<210	<500
		Used slag	510	48		50	500	113		30	
		Electrode	<50	122	40	<130	30	43	822	<100	
		Ingot 6/	<50	191		225	30	94		<100	
SA 26, 121 1/	Acid CaF ₂ 8/	Unused slag	310	432	150	20	<100	26		1500	18,700
		Used slag	390	45	350	30	1090	10		90	1200
		Electrode	<50	92		20	375	34	705	100	
		Ingot 5/	<50	96	14	375	45	58	954	250	
SA 26, 122 1/	Acid CaF ₂ 7/	Unused slag	350	76	500	160	2200	<10		1750	
	With TZM liner	Used slag	750	26	150	20	350	21		<20	1200
		Electrode	<50	92		20	375	34	705	100	
		Ingot 5/	75	82	26	275	50	67	667	250	
SA 26, 246 1/	Acid CaF ₂ 7/	Unused slag	440	137		80	<100	22		90	
	With TZM liner	Used slag	328	118		20	1100	20		<20	
	No Ti	Electrode	<50	92	20	375	250	34	705	100	
	Recycled top slags	Ingot 5/	<50	100	27	275	30	47	969	100	
SA 26, 207 2/	Acid CaF ₂ 8/	Unused slag	310	432	150	20	<100	26		1500	18,700
		Used slag	490	88	<140	60	5600	23		130	5400
		Electrode	450	64	66	425	4000	125	580	150	
		Ingot 5/	1500	47	146	500	110	133	1052	700	

(Continued)

TABLE 15. Impurity concentrations (ppm) in metal and slag phases before and after titanium electroslag melting (Continued)

Run	Slag	Impurities (Fluorine and chlorine analyses given in footnotes)									
		Al	C	CO ₂	H	Fe	Mg	N	O	Si	Ti
SA 26, 183 1/	MgF ₂ 7/	50	123	100		60		11		390	1700
	With TZM liner	250	75	400		90		32		200	15,600
	Ti	<50	92		20	375	250	34	705	100	
	Electrode	75	47		20	350	115	60	1198	175	
SA 26, 185 1/	4.0 wt % MgF ₂	80	29	300		110	18,700	<10		620	300
	in CaF ₂ 7/	140	62	300		60	6900	25		620	10,600
	With TZM liner	<50	92		20	375	250	34	705	100	
	No Ti	100	61		20	500	145	53	1150	400	
SA 26, 193 1/	12.3 wt % MgF ₂	190	74	100		80	30,000	<10		470	700
	in CaF ₂ 7/	500	198	210		<10	31,700	21		30	13,200
	No liner	<50	92		20	375	250	34	705	100	
	No Ti	200	72		21	450	145	73	814	400	
SA 26 250 1/	18.5 wt % SrF ₂	320	109			220	400	23		640	
	in CaF ₂ 7/	510	102			10	1600	22		<20	
	With TZM liner	<50	92		20	375	250	34	705	100	
	No Ti	<50	110		21	400	50	46	760	100	
SA 26, 198 1/	52.0 wt % LaF ₃	630	167	240		700	600	41		<50	1600
	in CaF ₂ 7/	570	58	100		60	1500	<45		80	17,900
	With TZM liner	<50	92		20	375	250	34	705	100	
	No Ti	150	84		19	500	110	69	501	300	

(Continued)

TABLE 15.- Impurity concentrations (ppm) in metal and slag phases before and after titanium electroslag melting (Continued)

Run	Slag	Impurities (Fluorine and chlorine analyses given in footnotes)						
		Al	C	Fe	H	Mg	N	O
SA 26, 319 1/	75.0 wt % LaF ₃ -	300	209	60		200	12	
	25.0 wt % CaF ₂ 7/	185	61	45		1500	18	
	With TZM liner	<50	92	375	20	250	34	705
	No Ti	100	92	225	23	90	50	870
SA 26, 294 1/	LaF ₃ 7/	<50	121	<50		10	11	
	With TZM liner	190	93	<15		800	18	
	No Ti	<50	92	375	20	250	34	705
	Electrode	<50	128	500	28	30	55	830
SA 26, 295 1/	LaF ₃ 7/	<50	372	<50		<10	23	
	With TZM liner	170	117	<30		1700	17	
	No Ti	<50	92	375	20	250	34	705
	Electrode	50	118	300	25	60	58	728
SA 26, 341 1/	50.0 wt % LaF ₃ -		636				11	
	46.0 wt % CaF ₂ -							
	4.0 wt % MgF ₂ 7/							
	With TZM liner	<50	92	375	20	250	34	705
(MgF ₂ used top slag from SA 26, 183)	No Ti	<100	125	400	18	135	45	791
	Electrode							
	Ingot 5/							
	Used slag							

(Continued)

TABLE 15.- Impurity concentrations (ppm) in metal and slag phases before and after titanium electroslag melting (Continued)

Run	Slag	Impurities (Fluorine and chlorine analyses given in footnotes)						
		Al	C	Fe	H	Mg	N	Si
SA 26, 398 2/ 10/	2 wt % Y in CaF ₂ 7/	10-1000	3530	---	---	3-30	22	300-3000
	Fused: no liner	---	182	---	---	10-3000	54	<30
	no T.	<50	92	375	20	250	34	100
	Electrode Ingot 5/	80	505	500	26	<50	49	597 300
SA 26, 399 1/ 10/	2 wt % Y in CaF ₂ 9/	294-2941	379	12-100	---	11-100	27	296-2942
	Blended	---	181	---	---	10-30,000	65	<30
	(CaF ₂ 7/fused	<50	92	375	20	250	34	100
	with no liner and no Ti)	60	106	400	26	<50	50	1327 300

- 1/ Magnesium-reduced, vacuum-distilled sponge used.
- 2/ Magnesium-reduced, leached and dried sponge used.
- 3/ Magnesium-reduced, gas-swept and/or water-leached sponge used
- 4/ Sodium-reduced, leached and dried sponge used
- 5/ Four-inch-diameter round ingot
- 6/ Slab-shaped ingot, 7" x 20".
- 7/ Fused in resistor furnace (remarks under slag indicate fusion conditions.)
- 8/ Fused in melting furnace.
- 9/ Values calculated from Y and CaF₂ analytical results.
- 10/ Furnace pumped to nominal vacuum at completion of run.

--- Not detected spectrographically.

(Continued)

TABLE 15.- Impurity concentrations (ppm) in metal and slag phases before and after titanium electroslag melting (Continued)

Run	Fluorine analyses		Material	Chlorine analyses	
	F (ppm)			Cl (ppm)	
SA 25, 897	...	...	Unused slag		440
SA 26, 061	85	...	Used slag		5200
SA 26, 077	260	...	Ingot		<115
SA 26, 084	207	...	Ingot		
SA 26, 158	115	...	Ingot		
SA 26, 159	...	...	Used slag		7900
SA 25, 835	120	...	Ingot		80
SA 25, 934	...	...	Used slag		8200
SA 26, 121	125	...	Ingot		<75
SA 26, 122	...	...	Used slag		21,000
SA 26, 207	189	...	Ingot		
SA 26, 183	137	...	Ingot		
SA 26, 185	130	...	Ingot		
SA 26, 193	150	...	Ingot		
SA 26, 198	85	...	Ingot		
SA 26, 319	300	...	Ingot		
SA 26, 294	90	...	Ingot		
SA 26, 295	110	...	Ingot		
SA 26, 398	125	...	Ingot		
SA 26, 399	70	...	Ingot		
SA 26, 399	85	...	Ingot		
SA 26, 399	70	...	Ingot		
SA 26, 399	65	...	Ingot		
SA 26, 399	<63	...	Ingot		

of the fused billets which had been crushed, split-sampled, and ground to minus-100 mesh. Analyses for the used slag are average of determinations on the split-sampled top slags and entire sidewall slag, both ground to minus-100 mesh. Metallic impurity concentrations were obtained from the average of two samples of as-received sponge, whereas gas impurities were analyzed on turnings and solid samples obtained from two to four vacuum-arc-melted buttons except for the magnesium-reduced gas swept and sodium-reduced leached and dried titanium, which were obtained from vacuum-arc-melted ingots. Ingot turnings provided the material for metallic impurity, chlorine, fluorine, carbon, and nitrogen analyses, and slices were used for oxygen and hydrogen ingot analyses. Average values for top and bottom ingot samples are shown. It must be remembered that in most cases, impurity concentration differences between unused and used slags, and electrode and ingot impurities of 100 ppm can be considered significant. These data include an air melt and a run made with a graphite liner in the crucible. The latter was used in order to reduce the thermal gradients across the melt. A portion of these data permit the evaluation of the partitioning of impurities between the metal and slag phases.

A distribution ratio (D) of a specific impurity between the slag and metal phases may be defined as the ratio of the impurity content of the used slag to that of the ingot. The result offers a measure of the slag's capability to remove unwanted impurities from the metal. In order to provide a basis for comparison

of D with the initial impurity concentrations in the slag and metal, a second distribution ratio (D'), defined as the ratio of impurity in the unused slag to that in the electrode, may be employed. Such calculations have been made using the data in table 15, and are shown in table 16. In general, a favorable impurity partitioning between the slag and metal is indicated by a significantly higher value of D relative to D' . Examination of tables 15 and 16 shows that regardless of slag composition, Si and N generally show unfavorable partitioning, although N is more favorably distributed when Y- CaF_2 slags are used. Invariably, Mg is favorably distributed between the slag and metal. With the exception of two runs using reagent-grade CaF_2 when melting magnesium-reduced and leached sponge, and LaF_3 slag, Al is generally unfavorably partitioned as is Fe except when a pure MgF_2 , acid-grade CaF_2 (with the same sponge), or LaF_3 slags are used. Carbon is also generally unfavorably distributed except when small amounts of MgF_2 are added to CaF_2 slag, in which case there is a favorable partition.

Additional analytical data on electrode material and resulting ingots are shown in table 17. All values were obtained in the same manner as described previously for those given in table 15.

It is evident from tables 15 and 17 that none of the slag compositions studied thus far effectively remove hydrogen from the metal, even though it was thought that MgF_2 might accomplish this. The same is true for oxygen despite the fact that there is generally an increase in CO_2 in the slag during the runs.

TABLE 10. - Impurity distribution ratios for slag and metal phases in the
electroslag melting of titanium

Run number	Distribution ratio	Impurities						
		C	Cl	Fe	Mg	N	O	Si
SA 25, 897	D	>9.07	0.66	>45.22	0.38	13.75	0.78	<0.31
	D'	>12.20	5.72	0.13	0.36	0.94		5.20
SA 26, 253	D	>8.90	3.06	0.44	96.86	0.39		>2.05
	D'	>13.20		0.53	5.33			>2.20
SA 26, 061	D	>6.00	3.47	0.10	<15.22	0.31	1.55	0.16
	D'	>3.40	14.00	0.17	~0	0.19	1.13	2.53
SA 26, 249	D	12.80	1.06	<0.03	30.91	<0.30		<0.13
	D'	>7.00	0.75	0.53	3.60	0.38		0.50
SA 26, 158	D	2.75	1.68	0.03	158.00	<0.15		0.25
	D'	0.31	3.13	0.07	0.33	0.14		5.07
SA 26, 159	D	0.70	1.46	>109.33	133.85	<0.13		<0.18
	D'	0.27	4.16	0.28	0.25	0.21		2.73
SA 25, 835	D	0.58			56.99	<0.16		
	D'	3.50	3.06	0.28		<0.22		>3.40
SA 25, 934	D	5.21	0.51	~0	17.33	<0.14		>0.50
	D'	>14.40	3.45	0.36	4.75	5.54		>4.80
SA 26, 157	D	>10.20	0.25	0.22	16.67	1.20		>0.30
	D'	>7.60	0.71	>0.54	35.00	0.44		~2.10
SA 26, 122	D	10.00	0.32	0.07	7.00	0.31		<0.08
	D'	>7.00	0.83	0.43	8.80	<0.29		17.50
SA 26, 121	D	>7.80	0.47	0.08	24.22	0.17		0.36
	D'	>6.20	4.70	0.05	<0.40	0.76		15.00
SA 26, 246	D	>6.56	1.18	0.07	36.67	0.43		<0.20
	D'	>8.80	1.49	0.21	<0.40	0.65		0.90
SA 26, 207	D	0.33	1.87	0.12	50.91	0.17		0.19
	D'	0.69	6.75	0.05	<0.03	0.21		10.00

(Continued)

TABLE 16.- Impurity distribution ratios for slag and metal phases in the
electroslag melting of titanium (Continued)

Run number	Distribution ratio	Al	C	Fe	Mg	N	Si
SA 26, 183	D	3.33	1.60	0.26		0.53	1.14
	D'	>1.00	1.34	0.16		0.32	3.90
SA 26, 185	D	1.40	1.02	0.12	47.58	0.47	1.55
	D'	>1.60	0.32	0.29	74.80	<0.29	6.20
SA 26, 193	D	2.50	2.75	<0.02	218.62	0.29	0.08
	D'	>3.80	0.80	0.21	120.00	<0.29	4.70
SA 26, 250	D	>10.20	0.93	0.03	32.00	0.48	<0.20
	D'	>6.40	1.18	0.59	1.60	0.68	6.40
SA 26, 198	D	3.80	0.69	0.12	13.64	<0.65	0.27
	D'	>12.60	1.82	1.87	2.40	1.21	<0.50
SA 26, 319	D	1.85	0.66	0.20	16.67	0.36	<0.18
	D'	>6.00	2.27	0.16	0.80	0.35	<0.40
SA 26, 294	D	>3.80	0.73	>0.03	26.67	0.33	0.01-0.05
	D'	~1.00	1.32	>0.01	0.04	0.32	~0
SA 26, 295	D	3.40	0.99	>0.10	28.33	0.29	0.01-0.05
	D'	~1.00	4.04	>0.01	>0.04	0.68	~0
SA 26, 341	D						
	D'		6.91			0.32	
SA 26, 398	D	~0	0.36	~0	>0.20->60.00	1.10	<0.10
	D'	>0.2->20.0	38.37	~0	0.01-0.12	0.65	3.00-30.00
SA 26, 399	D	~0	1.71	~0	>0.20->600.00	1.30	<0.10
	D'	>5.88->58.82	4.12	0.03-0.27	0.04-0.40	0.79	2.96-29.42

TABLE 17. - Impurity concentrations in electrode stock and electroslag-melted titanium ingots

Run	Slag	Impurities										7/
		Al	C	Cl	Fe	H	Mg	N	O	Si		
SA 26, 340 <u>1/</u>	5.0 wt % CaCl ₂ - Electrode	<50	92		375	20	250	34	705	100	Sn <240	
	95.0 wt % reag. Ingot	<65	96		400	36	75	41	909	350	Cu >5000	
(CaF ₂ <u>5/</u> with TZM liner and no Ti)	CaF ₂										Mn <75	
											Mo <65	
											Sn 350	
SA 26, 343 <u>1/</u>	10.0 wt % CaCl ₂ - Electrode	<50	92		375	20	250	34	705	100	Sn <240	
	90.0 wt % reag. Ingot	<50	91	<20	600	43	70	40	886	150	Cu 5000	
(CaF ₂ <u>5/</u> with TZM liner and no Ti)	CaF ₂										Sn <290	
SA 26, 344 <u>1/</u>	20.0 wt % CaCl ₂ - Electrode	<50	92		375	20	250	34	705	100	Sn <240	
	80.0 wt % acid Ingot	<50	90		600	45	50	34	954	175	Cu >5000	
(CaF ₂ <u>6/</u>)	CaF ₂										Sn 400	
SA 26, 347 <u>1/</u>	30.0 wt % CaCl ₂ - Electrode	<50	92		375	20	250	34	705	100	Sn <240	
	70.0 wt % acid Ingot	<50	96	<20	500	63	40	46	946	<100	Cu 3000	
(CaF ₂ <u>6/</u>)	CaF ₂											
SA 26, 364 <u>2/8/</u>	7.5 wt % CaCl ₂ - Electrode	450	64		425	66	4000	125	580	150		
	92.5 wt % reag. Ingot	400	77		550	210	80	122	823	200	Cu 2000	
(CaF ₂ <u>5/</u> with Tzm liner and no Ti)	CaF ₂											

(Continued)

TABLE 17.- Impurity concentrations in electrode stock and electroslag-melted titanium ingots (Continued)

Run	Slag		Impurities									
			Al	C	Cl	Fe	H	Mg	N	O	Si	Ti
SA 26, 384 $\frac{2}{8}$	23.0 wt % CaCl_2	Electrode	450	64		425	66	4000	125	580	150	
	77.0 wt % acid	Ingot	1000	54		500	213	100	121	917	300	Cu 2000
	CaF_2 ($\text{CaF}_2 \frac{6}{5}$)											
SA 26, 385 $\frac{1}{8}$	Reag. $\text{CaF}_2 \frac{5}{6}$	Electrode	<50	92		375	20	250	34	705	100	Sn <240
	TZM liner, no Ti	Ingot	50	89		400	21	80	40	1089	100	Mo 75 Sn 400 F 128
SA 26, 408 $\frac{1}{8}$	Recycled acid	Electrode	<50	92		375	20	250	34	705	100	Sn <240
	$\text{CaF}_2 \frac{6}{5}$	Ingot	60	87		450	22	<50	54	923	100	Mn 50 Sn 250
SA 26, 487 $\frac{3}{5}$	Acid $\text{CaF}_2 \frac{5}{6}$	Electrode	<50	178		500	18	400	50	500	<100	Cr 90 $\frac{9}{5}$ Mn 80
	No liner, no Ti	Ingot	35	125		900		35	59	2535	<55	Ni 50
SA 26, 488 $\frac{4}{5}$	Acid $\text{CaF}_2 \frac{5}{6}$	Electrode	<50	122		<130	40	30	43	822	<100	
	No liner, no Ti	Ingot	10	147		30		<5	48	1189	30	Cu 140

All values in ppm.

All ingots produced were four inches in diameter unless otherwise indicated. In all cases, CaCl_2 was fused in resistor furnace with Mo liner and no Ti; blended with fused CaF_2 before use.

(Continued)

TABLE 17. - Impurity concentrations in electrode stock and electroslag-melted
titanium ingots (Continued)

- 1/ Magnesium-reduced, vacuum-distilled sponge used.
- 2/ Magnesium-reduced, leached and dried sponge used.
- 3/ Magnesium-reduced, leached and/or gas-swept sponge used.
- 4/ Sodium-reduced and leached sponge used.
- 5/ Fused in resistor furnace (remarks under slag composition indicate fusion conditions.)
- 6/ Fused in melting furnace.
- 7/ Unless otherwise indicated, Ca, Cr, Cu, Mr., Mo, and V are all present in amounts <50 ppm; Ni <35 ppm; Pb <200 ppm; Sn <180 ppm in electrode and ingot.
- 8/ Furnace pumped to nominal vacuum at completion of run.
- 9/ Ingot impurities.

Two exceptions are when the 52 weight percent LaF_3 in CaF_2 and the fused 2 weight percent Y in CaF_2 slags were used wherein the oxygen content decreased substantially. The fluorine content in the metal melted under the Y- CaF_2 slag also appears to be reduced. It is to be noted that the MgF_2 slag increased about four times in oxygen content over CaF_2 . All slags for which data are available except acid-grade CaF_2 appear to pick up some titanium during the runs.

Data are given for several runs in tables 15 and 17 wherein the furnace atmosphere was evacuated to a nominal vacuum upon completion of the melt. Such procedure would presumably reduce gaseous impurities if these were not chemically or otherwise combined with the metal, and the evacuating atmosphere would act to carry off such impurities. A comparison of impurities in metal melted with and without such terminal evacuation can be made by consulting tables 15 and 17 and specifically runs SA 25, 897 and SA 26, 385 for reagent-grade CaF_2 , and runs SA 26, 121 and SA 26, 408 for acid-grade CaF_2 . Indications are that Si, C, and perhaps N are reduced by such procedure and that other impurities remain essentially unchanged.

The CaCl_2 used for the runs was isostatically pressed and treated in a similar manner as described previously for other slag compositions. A molybdenum liner was used in the resistor furnace for the fusion step. No titanium was added to the slag. This material was then added in the desired

proportion to fused CaF_2 and subsequently blended before use. These slags are difficult to handle because of the deliquescent nature of CaCl_2 , and must be kept at elevated temperatures at all times when not in use. In addition, the used slags are pyrophoric when removed from the furnace after a run.

Examination of the results in table 17 demonstrates that the addition of up to 30 weight percent CaCl_2 to CaF_2 slag does not improve the metallic impurity concentrations over that in titanium ingots melted under pure fluoride slags, with the exception of Si in metal melted under 30 weight percent CaCl_2 - CaF_2 slag, and Mg in metal melted under all chloride-fluoride slags. Noteworthy is the increase in copper taken up from the crucible. Although the carbon and nitrogen levels remain relatively stationary, there is an increase in oxygen and hydrogen in the melted metal. The hydrogen impurity content appears to be a function of the chloride concentration in the slag, and the increase in both the oxygen and hydrogen may be due to the deliquescent nature of CaCl_2 whereby these impurities are derived from the water which is retained by the slag. Upon removal from the crucible after the run, the used sidewall slag contained moisture and considerable copper from the crucible. As would be expected, titanium melted with chloride-containing slags appeared to be harder than that melted under pure fluoride slags. It is therefore not recommended that a chloride addition in the form of CaCl_2 be added to the slag despite the Russian contention (8), since whatever advantages may ensue (these appear to be confined to the smooth operating conditions alone) are largely offset by its obvious shortcomings.

It is apparent from tables 15 and 16 that both reagent- and acid-grade CaF_2 (runs SA 26, 249 and SA 26, 246, respectively) can be recycled at least once without adversely affecting the capability of the slag to take up impurities without contributing further impurities to the metal above that to be expected of unused slag. The recycling process consisted of crushing the used top slag from several small-scale runs, blending this mixture, followed by fusion in the resistor furnace in a TZM liner with no titanium chunks.

All of the slag compositions studied, with the exception of MgF_2 , MgF_2 - CaF_2 , LaF_3 , and MgF_2 - CaF_2 - LaF_3 , offered satisfactory operating conditions during the runs. The less stable nature of MgF_2 (see table 9), together with possible variations in physicochemical properties of this slag may account for the observed bumping, degassing, and resulting poorer ingot quality. When pure LaF_3 was used as a slag, there was a tendency for the slag to become entrapped in the metal. No doubt this is due to an unfavorable density differential between slag and metal (see table 9). Slags high in LaF_3 exhibit a tendency to freeze on the crucible sides and it was noted that especially the 25 weight percent CaF_2 -75 weight percent LaF_3 slag cooled extremely slowly after the power was shut off.

Metal melted under the 2 weight percent Y- CaF_2 slags developed exceptionally smooth and lustrous sidewalls, although the titanium showed a slight increase in hardness. The increase in ingot carbon in SA 26, 398 (see table 15) is attributed to the evident free graphite pickup during the fusion step. X-ray diffraction data indicate that the fused Y is probably present in some form to a

large extent in solution with CaF_2 in the unused slag but that less Y is present in solution with CaF_2 after melting. No evidence of segregated yttrium carbide or oxide is present in the used slag. The ingots showed some yttrium present (250 - 300 ppm), which is above the normal <50 ppm for metal melted under slags without yttrium additions. Noteworthy also is that the fluorine contents appear to be lower in Y- CaF_2 slag melted material.

No significant differences in impurity partitioning is evident as a function of ingot size. Reagent-grade CaF_2 appears to be just as passive a slag in the 7" x 20" slab-shaped melts as in the melting of 4-inch-round ingots. In addition, the use of acid-grade CaF_2 appears to be justified as a replacement for the reagent-grade material in terms of effective impurity removal from titanium metal.

The foregoing suggests certain alternatives which can be considered in the process of electroslag melting of titanium. It is obvious that if such slag compositions as MgF_2 , whose physicochemical properties differ substantially from CaF_2 , are used, different operating conditions must be employed. One difficulty which was experienced using this slag composition was a rough start. Evidently MgF_2 is not as thermally conductive as is CaF_2 , especially in the solid state. Rough starting could be alleviated by adding a molten slag at the beginning of the run. In this case the applied heat can be better used for initial metal melting. This points out that a basic knowledge of physicochemical proper-

ties of slags such as thermal and electrical conductivities would be extremely useful in evaluating optimum compositions and melting conditions. In order for process predictions to be more effective and to make maximum use of thermodynamic data in the literature, it would be advantageous to ascertain to what extent equilibrium is attained during the electroslag process. This could be effectively accomplished by a comparison of observed impurity partitioning between the slag and metal phases and the experimentally determined equilibrium distribution under the same temperature and physical conditions for the slag-metal systems under consideration. There are essentially no equilibrium or thermochemical data available on such systems as Ca-Ti-F, Mg-Ti-F, La-Ti-F, Sr-Ti-F, or combinations thereof upon which the approach to equilibrium during electroslag melting of titanium can be based. Systematic high-temperature, controlled-atmosphere studies involving these components would also establish the length of time necessary to attain equilibrium, and which form and composition of the starting materials are best suited. Implicit in the above is a precise evaluation of the temperatures involved during the melting process (a factor which is not well known at present, although the slag temperature appears to be normally slightly higher than that of the electrode material during melting) and the subsequent control of this temperature to as constant a value as possible so that thermodynamic predictions would have the maximum validity.

GENERAL COMMENTS AND CONCLUSIONS

Beginning in Fiscal Year 1968, the Bureau has conducted research on the problem of low-density inclusions which mysteriously appear in 1 to 2-percent of commercial ingots. As a part of the study, it was shown that synthetic nitride inclusions are more likely to remain intact through a single electroslag melt than through a single vacuum-arc melt. This observation is consistent with the general conclusion that the disappearance (dissolution) of the particles is favored in vacuum, at the highest power input, and when the pool volume is maximum.

Some comment is appropriate on the electrolytic effects in slag melting. The similarity between the electroslag-melting furnace and the fused-salt electrolytic cell is evident. Since the furnace is then a cell, we would expect the Ca^+ and the F^- ions in the conducting slag to migrate to the appropriate electrode and be freed. At the temperatures involved, both fluorine and calcium would be gaseous. Casual observation of the operation confirms this, as bright "beads" which are thought to indicate gas-phase conduction or arcing, are often seen at one or the other pole during melting. Free calcium or free fluorine were never observed however. The conduction in the furnace then is probably crucible (or ingot) to gas to molten slag to gas to molten electrode.

It was considered that perhaps the residual fluorine content (see above) in the ingot might be reduced if the fluorine ion (F^-) was released at the electrode rather than at the ingot slag interface. Analyses from reverse-polarity

melts do not bear out this contention. Possibly the conduction is, as suggested above, from crucible to slag rather than ingot to slag.

With the exception of the single test on columbium and the reported work on molybdenum (4), no further explorations have been made as to the utility of the electroslag process for other metals. Reports have been received on the application to copper (13) and chrome-bronze (18). The ferrous alloy and superalloy producers are deeply involved in electroslag melting, of course, but beyond these there may be other applications not yet realized.

Zirconium, because of its close relationship to titanium, comes to mind as a possible candidate. However, until the effects of residual fluorine in zirconium are clearly delineated, the approach must be conservative since zirconium's primary use is in water-moderated nuclear reactors. The same reasoning applies to hafnium.

Of particular interest in this program was a study of the possibility of substituting the slag cover entirely for atmosphere control; that is, eliminate the vacuum pumps. Review of the data suggests that, if specifications are not too strict, an argon flush plus a slag cover could be substituted for a pump-down step. The cost of argon then must be balanced against the investment in pumps. It should be noted that fluoride vapors are deleterious to mechanical pumps.

It has been the practice in the United States to disregard the hydrogen content of titanium sponge, since two (and possibly three) vacuum melting steps lie ahead. Therefore, it is with no apprehension that the sponge is leached in

aqueous solutions, and scrap, embrittled with hydrogen and crushed, is added to the consumable electrodes. It is apparently no great problem to vacuum melt such electrodes of sponge and scrap and obtain ingots having less than 35 ppm hydrogen ^{7/}. However, as the data above show, the electroslag process does not remove hydrogen. Therefore, before the industry can accept the new process, some additional effort will be needed to eliminate this impurity.

A second problem with the electroslag process, at least as practiced at the Bureau, is the poor sidewalls obtained on the large-scale ingots. It is apparent from the few large-scale heats made that poor sidewalls were related to high volatile content in the sponge, and, conversely, better sidewalls were obtained from vacuum-distilled sponge. It was not possible within the scope of the program to test numerous variations of crucible design, electrode geometry, slag depth, electrode-to-ingot gap, or power input to gain the best sidewall condition. It is likely that as more and more heats are processed the quality of the ingots will improve.

It has been the concept throughout the program that single electroslag melting might substitute for double or triple vacuum-arc melting. It is now seen that the exploitation of the advantage of the process hinges on the hydrogen content, sidewall quality, and finally on the use of the resultant metal in critical application. That is, until electroslag-melted titanium is tried in hardware items and found

^{7/} This low limit for ingot is accepted by the industry because additional hydrogen is usually gained during the forging and rolling processes.

to be satisfactory, it will not be "certified" as acceptable. On the other hand it will not be tried extensively until there is some degree of certainty of its satisfaction. The solution to this "chicken and egg" problem probably lies in gradual change.

Finally, comment should be made on the potential saving of the process in the event that the single electroslag melt concept could be adopted commercially. The titanium sponge production in 1967 was on the order of 30,000 tons or 60,000,000 pounds. The extra step in double arc melting probably costs something on the order of 20¢ per pound of ingot produced. Single electroslag melting would eliminate this cost. Slag costs would decrease the potential savings to perhaps one half that value for a possible saving of six million dollars.

APPENDIX I

Contents of a memorandum dated December 20, 1968 from David Schlain, Supervisory Chemical Research Engineer, College Park Metallurgy Research Center, to R. A. Beall, Project Coordinator, Metals Processing Projects, Albany Metallurgy Research Center:

"Corrosion tests were run with the titanium coupons provided by the Albany Metallurgy Research Center and described in memorandum from Mr. James T. Dunham dated May 24, 1968. Two sets of specimens were used. One group of specimens had been prepared from electroslog-melted ingot SA 25,904 T by cold rolling. The second group had been cold rolled from vacuum-arc remelted ingot SA 25,110 T. The electroslog-melted material contained 100 ppm of fluorine and the vacuum-arc remelted titanium did not contain any fluorine. Our chief objective was to determine if 100 ppm of fluorine had a substantial effect on the corrosion resistance of titanium.

Sample preparation and test procedures were those normally used for total immersion tests in our laboratory, except that the exposures were for 30 days and not the usual six days. The corrodents selected for this evaluation were air-aerated substitute ocean water, air-aerated 10 percent sulfuric acid, and helium-aerated 5-percent sulfuric acid. All tests were conducted at 35° C. Four replicates of each type of titanium were exposed in each solution, two coupons and 750 ml of solution per vessel.

The data obtained in these tests are summarized in the table which appears below.

TABLE 1. - Corrosion of titanium in substitute ocean water and sulfuric acid solutions at 35° C, 30-day tests

<u>Corrodent</u>	<u>Corrosion rate, mpy</u>	
	<u>Vacuum-arc remelted</u>	<u>Electroslag-melted</u>
S. O. W. (air)	0.0	0.0
10% H ₂ SO ₄ (air)	28.3 (26.1-30.1)*	27.3 (24.0-29.0)*
5% H ₂ SO ₄ (He)	16.6 (15.4-18.0)*	19.0 (18.1-19.8)*

* Range

The data show that electroslag-melted and vacuum-arc remelted titanium have essentially the same corrosion behavior in these environments. Both types of titanium are inert in substitute ocean water and corrode at moderate rates in the sulfuric acid solutions.

All specimens exposed in 5 and 10-percent sulfuric acid solutions acquired a roughened surface. When magnified, such a surface shows numerous, very shallow pits. One pair of electroslag-melted coupons immersed in 5 percent helium-aerated sulfuric acid acquired a somewhat different appearance. A number of long, shallow grooves were formed on the surfaces. These could be the result of undercutting.

The results of these tests certainly indicate that the presence of 100 ppm of fluorine does not reduce the corrosion resistance of titanium. However, I am of the opinion that your original concern about the possible effect of fluorine as an impurity should not be laid to rest for all time. Straumanis and his coworkers reported that titanium corroded at 2,200 mpy in 0.02N hydrofluoric acid and that 9.3 percent sulfuric acid solution containing ammonium fluoride in a concentration of 0.05 molar corrodes titanium at 2,000 mpy. It can be estimated that in our corrosion experiments the highest concentration of fluoride ions that could have been formed was 0.1 mg per liter, assuming that the entire 100 ppm of fluorine entered the solution as fluoride ions. This is about 4,000 times less concentrated than a 0.02N solution. A concentration of 0.1 mg per liter of fluoride evidently has no effect on the corrosion of titanium. Given material with 100 ppm it would be difficult indeed to attain a concentration of 0.02N in fluoride. However, we do not have reliable information about the effect of the fluoride ion in concentrations between 0.1 mg per liter and 0.02N.

Signed: David Schlain

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