

11-30-66

CEND - 3742 - 288

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

MASTER

VANADIUM
PURIFICATION

There is no objection from the patent
point of view to the publication or
dissemination of this document:

Robert Group (Brookhaven)

By *R.B. Potter*

FIRST QUARTERLY PROGRESS REPORT

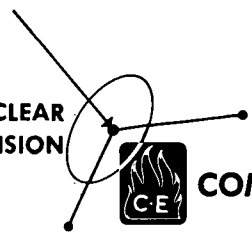
11/30 66

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:
A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.
As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Issued November 1966

NUCLEAR
DIVISION



COMBUSTION ENGINEERING, INC.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

~~COPYRIGHT~~

H.C. § 3.0 / MM

FOR OFFICIAL USE ONLY

PENDING PATENT CLEARANCE

CEND-3742-288
UC-25, Metals, Ceramics
and Materials
TID-4500, 48th Edition
CERN LIBRARY

H.C. \$3.00; MN 65

VANADIUM PURIFICATION

FIRST QUARTERLY

PROGRESS REPORT

For Period

July 1 to September 30, 1966

Prepared By:

S. Worcester, Wah Chang
S. S. Christopner, CEND

Contract AT(30-1)-3742
U.S. Atomic Energy Commission

Issued November 1966

Unclassified

Classification

W.M.H. Simon 11/66

Authorized Classifier Date

Approved by

W.P. Chernock

W. P. Chernock, Manager
Nuclear Laboratories

NUCLEAR DIVISION
COMBUSTION ENGINEERING, INC.
WINDSOR, CONNECTICUT

EXTERNAL DISTRIBUTION	No. of Copies
Mr. J. Edward Fox Fuels and Materials Branch U.S. Atomic Energy Commission Division of Reactor Development and Technology Washington, D. C. 20545	2
Mr. Jules M. Simmons, Chief Fuels and Materials Branch U.S. Atomic Energy Commission Division of Reactor Development and Technology Washington, D. C. 20545	1
Mr. K. A. Trickett Fuels and Materials Branch U.S. Atomic Energy Commission Division of Reactor Development and Technology Washington, D. C. 20545	1
Dr. Glenn W. Wensch, Chief Liquid Metal Projects Branch U.S. Atomic Energy Commission Division of Reactor Development and Technology Washington, D. C. 20545	1
U.S. Atomic Energy Commission New York Operations Office 376 Hudson Street New York, New York 10014 Attention: Development Contracts Division	1
U.S. Atomic Energy Commission New York Operations Office 376 Hudson Street New York, New York 10014 Attention: NYO Library	1
Mr. H. S. Potter, Chief New York Patents Group U.S. Atomic Energy Commission Brookhaven Office Upton, New York 11973	1
U.S. Atomic Energy Commission Division of Technical Information Extension Post Office Box 62 Oak Ridge, Tennessee 37830	1
Mr. A. J. Alexander U.S. Atomic Energy Commission HWOCR - Hartford Branch Post Office Box 500 Windsor, Connecticut 06095	1

EXTERNAL DISTRIBUTION (Continued)	No. of Copies
Mr. Leo Graup, Authorized Representative U.S. Atomic Energy Commission New York Operations Office 376 Hudson Street New York, New York 10014	1
Mr. L. Kelman Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois	1
Mr. J. H. Kittel Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois	1
Mr. R. E. Macherey Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois	1
Mr. R. M. Mayfield Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois	1
Dr. D. H. Gurinsky Brookhaven National Laboratory Upton, L.I., New York 11973	1
Mr. R. D. Baker Los Alamos Scientific Laboratory Los Alamos, Mexico	1
Mr. P. Patriarca Oak Ridge National Laboratory Post Office Box X Oak Ridge, Tennessee	1
Mr. W. O. Harms Oak Ridge National Laboratory Post Office Box X Oak Ridge, Tennessee	1
Mr. T. T. Claudson Pacific Northwest Laboratory Battelle Memorial Institute Post Office Box 999 Richland, Washington 99352	1

EXTERNAL DISTRIBUTION (Continued)	No. of Copies
Mr. S. J. Paprocki Battelle Memorial Institute Columbus, Ohio	1
Mr. O. N. Carlson Iowa State University Institute of Atomic Research Ames, Iowa	1
Mr. D. J. McPherson IIT Research Institute 10 West 35th Street Chicago, Illinois 60616	1
Mr. R. J. Van Thyne IIT Research Institute 10 West 35th Street Chicago, Illinois 60616	1
Mr. C. E. Weber Atoms International, Inc. Canoga Park, California	1
Mr. L. R. Weissert Babcock & Wilcox Company Atoms Energy Division Lynchburg, Virginia	1
Mr. E. L. Zebroski General Electric Laboratory Vallecitos Atomic Laboratory Post Office Box 1131 San Jose, California	1
Mr. J. A. McGurty General Electric Company Cincinnati, Ohio	1
Mr. R. C. Werner Mine Safety and Appliance Company 230 North Braddock Avenue Pittsburgh, Pennsylvania 15208	1
Mr. K. Puechl Nuclear Materials and Equipment Corporation Apollo, Pennsylvania	1
Mr. A. Strasser United Nuclear Corporation Fuels Division New Haven, Connecticut	1

CEND-3742-288
UC-25, Metals, Ceramics
and Materials
TID-4500, 48th Edition

EXTERNAL DISTRIBUTION (Continued)

No. of Copies

Dr. R. J. Allio
Westinghouse Electric Corporation
Atomic Power Department
Post Office Box 1075
Pittsburgh, Pennsylvania

1

VANADIUM PURIFICATION

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
I	100-Hour Rupture Stress of Tantalum and Niobium at $0.45 \times$ Homologous Temperature	5
II	Composition of Vanadium Granules	13
III	Material Balance of Arc Melted Vanadium Buttons	14
IV	Material Balance of Electron Beam Melted Vanadium Buttons	15
V	Hardness Values and Impurity Level of Buttons After Arc Melting	17
VI	Hardness Values and Impurity Level of Buttons After Electron Beam Melting	18

VANADIUM PURIFICATION

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>
1	Effect of Oxygen on the Tensile Strength of Niobium at Various Temperatures
2	Vanadium Purification Work Program
3	Effect of Gettering Element on Impurity Content
4	Vanadium Granules After Arc Melting
5	Vanadium With 1.5% Aluminum After Arc Melting
6	Vanadium With 1.5% Silicon After Arc Melting
7	Vanadium With 1.5% Yttrium After Arc Melting
8	Vanadium Granules After Arc Melting and Electron Beam Melting
9	Vanadium With 1.5% Aluminum After Arc Melting and Electron Beam Melting
10	Vanadium With 1.5% Silicon After Arc Melting and Electron Beam Melting
11	Vanadium With 1.5% Yttrium After Arc Melting and Electron Beam Melting

VANADIUM PURIFICATION

by

S. Worcester and S. S. Christopher

ABSTRACT

During the present quarter, a series of experiments was conducted in order to determine the most effective gettering element for purifying high interstitial vanadium. The gettering elements evaluated were aluminum, silicon, and yttrium. In addition to the preparation of unalloyed button melts of vanadium, alloys containing 0.5, 1.0, and 1.5 wt% of each of the gettering elements were melted. For every composition, two buttons were arc melted. One button of each composition was subsequently remelted in an electron beam button furnace. All buttons were then evaluated for chemical composition, room temperature hardness, and microstructure. Preliminary data from this phase of the program are discussed.

I. SUMMARY

The program is divided into three tasks: Task I, Melting Studies, Task II, Fabrication and Mechanical Testing and Task III, Weldability. The objectives of each of the three tasks are:

Task I, Melting Studies

To develop a commercial melting process for producing high purity vanadium.

Task II, Fabrication and Mechanical Testing

To assess the mechanical properties of a vanadium alloy produced from high purity feed material.

Task III, Weldability

To assess the weldability of a vanadium alloy produced from high purity vanadium feed material.

During this quarter, a series of button melts were made to determine the effects of aluminum, silicon and yttrium as gettering agents in vanadium. The buttons were produced by nonconsumable arc melting and electron beam melting and were evaluated for hardness and interstitial impurity level. Preliminary results indicate the following:

1. Of the three gettering agents, yttrium was found to be the most effective for scavenging oxygen from vanadium.
2. All three gettering agents were ineffective in reducing the nitrogen content of vanadium.
3. Silicon was the least satisfactory gettering agent for all interstitials and was not effectively removed by electron beam melting.

4. Electron beam melting removes interstitial carbon which combines with oxygen to form CO or CO₂. However, yttrium was found to hinder this reaction.

During the next quarter, approximately six ingots will be melted in production arc melting and electron beam melting furnaces. The ingots will be three inches in diameter by eight inches long and will permit evaluation of the melting techniques and gettering agents that proved most effective during Phase 1 of this task. The ingot length to diameter ratio corresponds to that of commercial ingots.

II. INTRODUCTION

Of all the refractory metals, vanadium appears to be the best suited, from a neutron economy point of view, for use in liquid metal cooled fast-breeder reactors. The reason for the superiority of vanadium over other refractory metals is the considerably lower neutron absorption cross section for vanadium which results in advantages with respect to safety, breeding ratio and doubling time. Although austenitic stainless steels represent the best current day potential for use as cladding in LMFBR systems, problems have been encountered and are associated with a loss in elevated temperature ductility. It is believed that this elevated temperature ductility problem is associated with helium formation (n, α reactions) and that the homologous temperature of the cladding will be an important controlling factor. Vanadium has a homologous temperature of 1470°F which is greater than the maximum cladding temperatures being considered for liquid metal cooled fast-breeder reactors. Vanadium base alloys appear to be suitable candidate cladding material alternatives to stainless steel for use in liquid metal cooled fast-breeder reactors.

The potential of vanadium alloys as a fast reactor fuel element cladding was first recognized by Smith and Van Thyne.⁽¹⁾ They based their selection of the strength of vanadium at elevated temperatures, its sodium compatibility, relatively high thermal conductivity, and ease of fabrication. More recently, Okrent⁽²⁾ has shown the advantage of vanadium over niobium and other refractory alloys for large fast-breeder reactors.

One basic problem in the use of vanadium alloys, however, is a high interstitial level, which can affect corrosion, compatibility, mechanical properties and fabrication.

The body-centered cubic materials, (V, Nb, Ta, W and Mo) are susceptible to embrittlement by the interstitial elements, oxygen, nitrogen, hydrogen and carbon. With proper control and distribution of specific interstitials, however, it is possible to impart improved mechanical properties, corrosion resistance, and compatibility to these materials.

In any study involving the body-centered cubic materials, extreme care must be taken to isolate the interstitials as a variable. Erroneous test results often occur if proper control of interstitials is not exercised. The effect of interstitials on the properties and performance of refractory metals are summarized below and emphasize the need for an understanding of their role in vanadium alloy technology.

A. Mechanical Properties

Normally, an increase in the interstitial level results in higher tensile strengths and lower elongations. Figure 1* illustrates the effect of oxygen on the tensile strength of niobium at various temperatures.

Interstitials not only affect short-time mechanical properties, but also influence the time-dependent properties such as creep and stress-rupture strength. Low interstitial material has a lower strength and a higher elongation than high interstitial material. This is demonstrated in Table I, which compares the 100-hour rupture life of high purity niobium and tantalum (electron beam melted) with powder metallurgy material.

*From Reference 3

TABLE I

100-HOUR RUPTURE STRESS OF TANTALUM AND NIOBIUM

AT 0.45 X HOMOLOGOUS TEMPERATURE

<u>Material</u>	<u>Stress (psi)</u>	<u>Interstitial Content (ppm)</u>
Niobium, Electron Beam	7,000	300
Niobium, Powder Metallurgy	17,000	600-700
Tantalum, Electron Beam	3,000	50
Tantalum, Powder Metallurgy	10,000	400-500

The results clearly demonstrate the degree of strengthening that can be obtained by the addition of interstitials. A large portion of the creep strength of the V-20 wt% Ti alloy may be attributed to its high concentration of interstitials, which range from 800 to 1100 ppm.

B. Liquid Metal Compatibility

Interstitials also play a role in the corrosion behavior of the refractory metals. Hoffman⁽⁴⁾ and others who studied the compatibility of the Nb-Li system demonstrated that the attack on niobium by lithium increases as a function of the oxygen present in the niobium prior to testing. Lithium has a greater affinity for oxygen than niobium and scavenges it from the cladding. Potassium and sodium, on the other hand, lose oxygen to niobium which can become embrittled as a result.

The interplay of the interstitials in the alloy and in the liquid metal becomes even more complex depending upon whether the interstitial is in solid solution or precipitated. Thus, weight gains or losses can occur in the same alloy with the same total interstitial level tested under identical conditions. The necessity of obtaining compatibility data on highly controlled pure metals and alloys cannot be overstressed. The individual effect of each interstitial on liquid metal compatibility should be established for each cladding - liquid metal system from the point of view of cladding embrittlement and mass transfer. Initial trends indicate improved performance for alloys with low total interstitials.

C. Fuel Compatibility

In view of the potential use of mixed plutonium-uranium oxide, carbide and nitride fuels in fast-breeder reactors, the compatibility of the fuel and the cladding must be established. In the fast-breeder reactor systems, the fuel-cladding interface may operate at temperatures as high as 700°C to 800°C. At these temperatures, interstitials may diffuse across the fuel-cladding interface and could lead to changes in fuel stoichiometry, embrittlement of the cladding and, if the interstitials diffuse through the cladding, problems of compatibility with the coolant.

ANL⁽⁵⁾ report that compatibility between vanadium and uranium-plutonium containing alloys is sensitive to the oxygen content of the vanadium. V-10 wt% Ti and V-20 wt% Ti were penetrated more deeply by the fuel than was vanadium; the difference in penetration between the titanium containing alloys and pure vanadium was attributed to lower oxygen contents (600 ppm) or the titanium itself. Thus, there is some indication that the development of a low oxygen vanadium and vanadium base alloy will lead to improved fuel-clad compatibility.

D. Fabrication Potential

For many years, the refractory metals were considered extremely difficult to fabricate. The state of early technology was such that both niobium and tantalum had to be fabricated by powder metallurgy processes that could not adequately reduce interstitial levels. With the development of electron beam melting and vacuum technology, these restrictions no longer apply. Presently, such low interstitial materials are readily fabricated at room temperature with conventional equipment.

Vanadium and some vanadium alloys can be fabricated at room temperature. Rolling of sheet and drawing of tubing of the V-20 wt% Ti alloy is performed at room temperature despite the relatively high interstitial content of the alloy. It seems reasonable to expect that with a lower interstitial level, higher reductions in percent of cold work could be taken between anneals, resulting in reduced fabrication costs.

On the basis of these considerations, a program aimed at reducing the interstitial level of vanadium was undertaken at CEND, with Wah Chang as the subcontractor.

III. PROGRAM SCOPE

The objectives of this program are as follows:

1. Development of a commercial melting process for producing high purity vanadium.
2. Determination of the mechanical properties of a vanadium alloy produced from high purity vanadium feed material.
3. Determination of the weldability of a vanadium alloy produced from high purity vanadium.

The program will be conducted under three tasks, namely Melting Studies, Fabrication and Mechanical Testing, and Weldability, which are subdivided into various phases of study. A program schedule is shown on Figure 2.

Task I, Melting Studies, will comprise three phases, (1) Screening Evaluations, (2) Secondary Scale-up and (3) Scale-up to commercial practice. In Phase 1, which is completed and will be described in detail later in this report, the effect of gettering agents such as aluminum, silicon, and yttrium was evaluated by melting small button ingots. Nonconsumable arc melting and electron beam melting were used to produce the button ingots and served as a screening process for the development of an optimum melting technique. The button ingots produced were analyzed for hardness, microstructure and interstitial level.

Phase 2 of Task I will utilize previously obtained data for production of a series of ingots approximately three inches in diameter by eight inches in length. These ingots will be melted in commercial consumable arc melting furnaces and electron beam furnaces. Since the diameter to length ratio of the ingots is representative of commercial practice, it should be possible to arrive at a purification process that can be readily scaled to commercial ingot sizes. The ingots from this phase will also be evaluated for purity, hardness and microstructure.

The third phase of Task I will be aimed at producing a vanadium ingot weighing approximately 100 lb and containing less than 500 ppm total interstitial with no interstitial over 300 ppm. The ingot must meet commercial standards with respect to porosity, cracks, and second phases.

Upon successful completion of Task I, a vanadium alloy selected by the Atomic Energy Commission will be melted and fabricated into sheet for testing by CEND and other AEC contractors.

Under Task II, CEND will perform tensile tests on sheet specimens at room temperature, 600 and 800°C, and on welded sheet specimens at room temperature and 800°C. The sheet specimens will be tested in the fully recrystallized and optimum heat treated conditions. The welded specimens will be tested in the as-welded or heat treated conditions.

In order to assess the effect of the lower interstitial content on the alloy, stress-rupture and creep properties will be determined in the 600 to 800°C temperature range. The test parameters will be selected to provide data which can be directly compared with available information on the high interstitial alloy.

Under Task III, the weldability of the low interstitial vanadium alloy will be evaluated using the tungsten inert gas (TIG) and electron beam welding process. TIG welds will be made without and with filler metal of the same composition as the base metal. Room temperature bend tests will be used to evaluate the as-welded, and as-welded and heat treated specimens. Specimens will also be evaluated for microstructure, hardness and mechanical properties.

IV. RESULTS OF EXPERIMENTAL EFFORT ON PHASE 1 OF TASK I

During this quarter, the effects of the gettering agents aluminum, silicon and yttrium were evaluated. Vanadium specimens with three concentration levels of each gettering element were prepared. The typical chemical composition of the vanadium granules used to prepare the specimens is shown in Table II.

The amount of gettering element added to the vanadium was arbitrarily selected as 0.5 wt%, 1.0 wt% and 1.5 wt%. These levels are in excess of the amount required to remove all the oxygen present in the alloy.

Aluminum wire, silicon chunks and yttrium buttons were the initial materials used in this experiment. The analyses of these materials are not complete at the present time and will be included in a later report.

Two 100-gr buttons of each composition were melted under a positive pressure of gettered argon in a nonconsumable tungsten arc furnace. One button was evaluated for chemistry, hardness and microstructure in order to study its properties after arc melting. The second button was electron beam melted and evaluated in a similar fashion. Two unalloyed vanadium control buttons were also prepared and evaluated. The experimental procedure and results obtained to date are described below:

TABLE II

COMPOSITION OF VANADIUM GRANULES

Impurities	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>Fe</u>	<u>Si</u>
Percent	0.021	0.0017	0.130	0.029	0.05	0.100

A. Arc Melting of Buttons

The gettering elements were broken into pieces 1/4 inch or smaller. In the furnace, the vanadium granules (all of which were less than 1/4 inch in diameter) were arranged so as to enclose the gettering material in order to hold splattering of the gettering addition to a minimum.

Every button was melted four times and turned over after each melting.

Table III shows the material balances of the buttons after arc melting. The data presently available do not permit discrimination of the relation between melting loss and the amount of gettering material. However, the melting loss can be expected to increase with the amount of volatile gettering element.

B. Electron Beam Melting of Buttons

Half of the twenty buttons (one button for each composition) were remelted in an electron beam button furnace designed and built by the U. S. Bureau of Mines.⁽⁶⁾ Each button was melted in a vacuum of 2×10^{-4} torr at a power of 20 kw for ten minutes. The material balances are shown in Table IV.

TABLE III

MATERIAL BALANCE OF ARC MELTED VANADIUM BUTTONS

Button Number	Vanadium (gr)	Gettering Element (gr)	Total (gr)	Weight After Arc Melting	Percentage of Loss
1 A	100.0		100.0	96.50	3.50
B	100.0		100.0	98.60	1.40
2 A	99.5	0.5 Al	100.0	94.85	5.15
B	99.5	0.5 Al	100.0	98.85	1.15
3 A	99.0	1.0 Al	100.0	92.45	7.55
B	99.0	1.0 Al	100.0	94.95	5.05
4 A	98.5	1.5 Al	100.0	98.35	1.65
B	98.5	1.5 Al	100.0	98.65	1.35
5 A	99.5	0.5 Si	100.0	98.40	1.60
B	99.5	0.5 Si	100.0	99.20	0.80
6 A	99.0	1.0 Si	100.0	99.55	0.45
B	99.0	1.0 Si	100.0	99.70	0.30
7 A	98.5	1.5 Si	100.0	97.35	2.65
B	98.5	1.5 Si	100.0	97.85	2.15
8 A	99.5	0.5 Y	100.0	98.40	1.60
B	99.5	0.5 Y	100.0	97.95	2.05
9 A	99.0	1.0 Y	100.0	97.13	2.87
B	99.0	1.0 Y	100.0	97.75	2.25
10 A	98.5	1.5 Y	100.0	98.60	1.40
B	98.5	1.5 Y	100.0	98.50	1.50

TABLE IV

MATERIAL BALANCES OF ELECTRON BEAM MELTED VANADIUM BUTTONS

Power, 20kw - Melting Time, 10 min - Vacuum, 2×10^{-4} torr

Button Number	Nominal Composition	Weight Balance (grams)			
	 Before EB After EB Loss Percentage
1B	V	76.6	68.4	8.2	10.7
2B	V-0.5Al	85.0	75.0	10.0	11.75
3B	V-1Al	75.7	66.9	8.8	11.6
4B	V-1.5Al	85.5	75.2	10.3	12.05
5B	V-0.5Si	80.4	71.6	8.8	10.95
6B	V-1.0Si	85.1	75.7	9.4	12.4
7B	V-1.5Si	85.4	76.2	9.2	10.8
8B	V-0.5Y	81.1	70.2	10.9	12.8
9B	V-1.0Y	79.8	71.4	8.4	10.5
10B	V-1.5Y	87.6	78.7	8.9	10.2

V. DISCUSSION OF RESULTS

A. Chemical Analyses and Hardness Data

Tables V and VI and Figure 3 show the DPH (10 Kg) hardness and analytical data obtained to date for all buttons after arc melting and electron beam melting. These results are discussed in relation to the gettering elements employed.

1. Vanadium Without Gettering Agent

As shown in Figure 3, electron beam melting lowered the hardness from 197.2 to 141.4 DPH and significantly reduced the oxygen and carbon contents of the pure vanadium button, viz., 0.046 wt% and 0.025 wt%, respectively. The slight increase (0.002 wt%) in nitrogen content confirms previous work indicating that electron beam melting does not reduce the nitrogen content. (7, 8)

2. Aluminum Getter

After arc melting, the hardness of the buttons doped with aluminum had increased with the aluminum content. This hardening is due to the formation of solid solutions of aluminum in vanadium. The hardness of every button had decreased after electron beam melting to fairly uniform levels, averaging about 135 DPH. The lowest hardness for aluminum gettering (131.5 DPH) was observed for a 0.5 wt% aluminum addition.

Aluminum was found to have slightly reduced the oxygen content in almost all cases of arc melting. After electron beam melting, the buttons with 0.5 wt% and 1.0 wt% aluminum also exhibited less oxygen content than the pure vanadium sample; however, the oxygen content of the button containing 1.5 wt% aluminum was 0.031 wt% above that of the pure vanadium button. This apparent inconsistency has not yet been resolved.

TABLE V

HARDNESS VALUES AND IMPURITY LEVEL OF BUTTONS AFTER ARC MELTING

Button Number	Nominal Composition	Hardness DPH	Impurities (wt%)					
			<u>O</u>	<u>N</u>	<u>C</u>	<u>Al</u>	<u>Si</u>	<u>Y</u>
1A	V	197.2	0.136	0.029	0.048	----	----	----
2A	V-0.5Al	199.0	0.120	0.025	0.035	0.22	----	----
3A	V-1.0Al	207.2	0.116	0.044	0.042	0.56	----	----
4A	V-1.5Al	215.5	0.131	0.026	0.043	1.28	----	----
5A	V-0.5Si	219.4	0.144	0.027	0.051	----	0.63	----
6A	V-1.0Si	241.4	0.149	0.018	0.062	----	1.30	----
7A	V-1.5Si	263.2	0.144	0.032	0.069	----	1.75	----
8A	V-0.5Y	134.8	0.031	0.035	0.041	----	----	0.11
9A	V-1.0Y	103.4	0.003	0.024	0.036	----	----	0.44
10A	V-1.5Y	93.2	0.008	0.034	0.041	----	----	0.70

TABLE VI
HARDNESS VALUES AND IMPURITY LEVEL
OF BUTTONS AFTER ELECTRON BEAM MELTING

Button Number	Nominal Composition	Hardness DPH (10kg)	Impurities (wt%)					
			<u>O</u>	<u>N</u>	<u>C</u>	<u>Al</u>	<u>Si</u>	<u>Y</u>
1B	V	141.4	0.046	0.034	0.025	----	----	----
2B	V-0.5Al	131.5	0.044	0.032	0.022	0.03	----	----
3B	V-1.0Al	133.2	0.033	0.034	0.018	0.12	----	----
4B	V-1.5Al	140.5	0.077	0.032	0.019	0.60	----	----
5B	V-0.5Si	158.3	0.018	0.034	0.030	----	0.77	----
6B	V-1.0Si	158.0	0.137	0.031	0.030	----	1.13	----
7B	V-1.5Si	186.3	0.064	0.023	0.037	----	1.14	----
8B	V-0.5Y	130.3	0.034	0.031	0.021	----	----	<0.0010
9B	V-1.0Y	121.5	0.017	0.029	0.033	----	----	<0.0010
10B	V-1.5Y	127.1	0.012	0.029	0.045	----	----	<0.0010

The analytical data indicate that aluminum does not have a scavenging effect on nitrogen. The carbon content of the aluminum gettered buttons was reduced both after arc melting and after electron beam melting. The electron beam melted button with 1.0 wt% aluminum had the lowest carbon content (0.018 wt%) of all gettering compositions.

3. Silicon Getter

From the increased hardness data for the silicon concentrations shown in Table V, it appears that silicon formed solid solutions with vanadium after arc melting in all three silicon concentrations.

After electron beam melting, the hardness values and carbon contents, although less than the values for the corresponding arc melted buttons, were higher than those for the electron beam melted pure vanadium button. Hardnesses and carbon contents increased with increasing silicon doping both for arc melted and electron beam melted buttons. The increasing carbon contents are probably caused by high carbon in the added silicon.

The oxygen and nitrogen data from the silicon-gettered samples are inconsistent.

An interesting data point from silicon doping is the electron beam melted 1.5 wt% silicon button which shows the lowest nitrogen content (0.023 wt%) of all arc melted and electron beam melted buttons. It is also interesting to note that the nitrogen curve for silicon-doped, electron beam melted buttons consistently shows decreasing nitrogen with increasing silicon. This desirable effect is offset, however, by the difficulty with which silicon is removed by electron beam melting.

4. Yttrium Getter

The hardness of yttrium-doped buttons decreased with increasing yttrium doping in the arc melted buttons, which confirms the work of Zwicker.⁽⁹⁾ After electron beam melting, the yttrium-doped buttons were softer than the corresponding pure vanadium button. However, the electron beam melted buttons with 1.0 wt% yttrium and 1.5 wt% yttrium showed an increase in hardness over the corresponding arc melted buttons. The three electron beam melted specimens showed a fairly uniform range of hardness (DPH 120 to 130) and all contained less than 0.001 wt% yttrium.

The hardness increase could be explained either by the loss of yttrium or by the carbon pickup (Table VI). It should be noted that this increase in hardness after removal of yttrium has been observed in all work conducted at Wah Chang and is felt to be due, at least in part, to the return of interstitial elements into solid solution.

The increase in carbon content is most likely due to intermittent backstreaming of diffusion pump oil. The presence of yttrium inhibits removal of carbon during electron beam melting. This can probably be explained by the strong affinity of yttrium for oxygen, which would reduce the oxygen available for reaction with carbon to form CO or CO₂. (Gibb's free energy of formation at 2000°F for CO is -68.750 cal/mol. For CO₂ it is -95.000 cal/mol and for Y₂O₃, -309.500 cal/mol).⁽⁴⁾

B. Metallography

The microstructures of the arc melted buttons are shown in Figures 4 through 7, and of the arc melted and electron beam melted buttons in Figures 8 through 11.

The difference between the second-phase structures in the yttrium gettered buttons and in the other buttons is quite significant. Where yttrium was used, the second phase had formed into randomly dispersed semi-spherical particles, probably consisting mainly of yttrium oxide. These semi-spherical globules should lead to more ductility than would be expected of the other specimens which contain second-phase precipitate stringers.

The vanadium-yttrium binary phase diagram⁽¹⁰⁾ shows that there is a very large miscibility gap in the liquid region and that the liquid vanadium phase has almost no solubility for the liquid yttrium phase. This lack of liquid miscibility could explain the globular nature of the second-phase particles and the peculiar grain boundary behavior evident in Figure 4. During arc melting, two liquid phases are formed and the yttrium-rich phase proceeds to getter oxygen because the yttrium oxides have a more highly negative Gibbs free energy of formation than the vanadium oxides.⁽¹¹⁾ The yttrium oxide-rich phase or mixture probably forms into globules due to high surface tension.

VI. CONCLUSIONS

The following conclusions can be drawn from the experimental work in Phase 1:

1. Yttrium proved to be more effective than silicon or aluminum as a gettering element for scavenging oxygen in vanadium. Yttrium was also most effective in softening arc melted and electron beam melted buttons.
2. It has been shown that neither of the evaluated three gettering elements can effectively decrease the nitrogen content in vanadium. However, low nitrogen feedstock is available.
3. Silicon was not effectively removed by electron beam melting. The silicon-doped specimens remained higher in carbon after electron beam melting than did the aluminum-doped buttons.
4. Chemical analyses indicated essentially complete removal of yttrium after electron beam melting, whereas substantial levels of silicon and aluminum were left in electron beam melted buttons.
5. Carbon is removed during electron beam melting by combination with O_2 to form CO or CO_2 . The addition of yttrium appears to hinder the CO or CO_2 formation.
6. 1.0% yttrium additions reduced the interstitial (C, N_2 , O_2) content after arc and electron beam melting from 1800 ppm to 790 ppm.

VII. FUTURE WORK

Based on the results obtained in Phase 1, the following series of tests is planned in order to produce vanadium having a total interstitial level of less than 500 ppm.

Low nitrogen vanadium granules (<200 ppm N) will be pressed into compacts and electron beam melted without the addition of any gettering element. This will allow the oxygen to react with carbon to form CO or CO₂, thus reducing the carbon level of the ingot. This ingot, which should be low in carbon, hydrogen and nitrogen, but high in oxygen, will then be arc melted with yttrium added as the gettering agent. The yttrium should scavenge the oxygen and reduce the oxygen concentration. A second electron beam melt may be made to remove the residual yttrium in the arc melted ingot. Approximately six ingots, three inches in diameter by eight inches long, will be melted.

REFERENCES

1. Smith, K. F., and Van Thyne, R. J., "Selected Properties of Vanadium Alloys for Reactor Applications," ANL 5661, May 1957
2. Okrent, D., "Nuclear Considerations in the Selection of Materials for Fast Power Reactors," (AIME) IMC Special Report Series, No. 12, 1963
3. Vaughan, H. G., and Rose, R. G., "The Tensile Properties of Columbium," UKAEA, IGR-TN (C-583), November 1958
4. DiStefano, J. R., and Hoffman, E. E., "Corrosion Mechanisms in Refractory Metal Systems," ORNL 3424, September 1963
5. Adams, R. M., and Glassner, A., "Reactor Development Program Progress Report," ANL-6840, January 1964
6. Anable, W., and Beall, R., "Report of Investigation No. 6341," U. S. Bureau of Mines
7. Carlson, O. N., "High Purity Vanadium," Journal of Metals, p. 320, March 1966
8. Anable, W., Albany Division, U. S. Bureau of Mines, Private Communication, August 1966
9. Zwicker, Ulrich, German Patent 1,030,036, 14 September 1954
10. Elliott, R. P., Constitution of Binary Alloys, McGraw-Hill Book Company (1965)
11. Wicks, C. E., and Block, F. E., Bulletin 605, Bureau of Mines (1963)

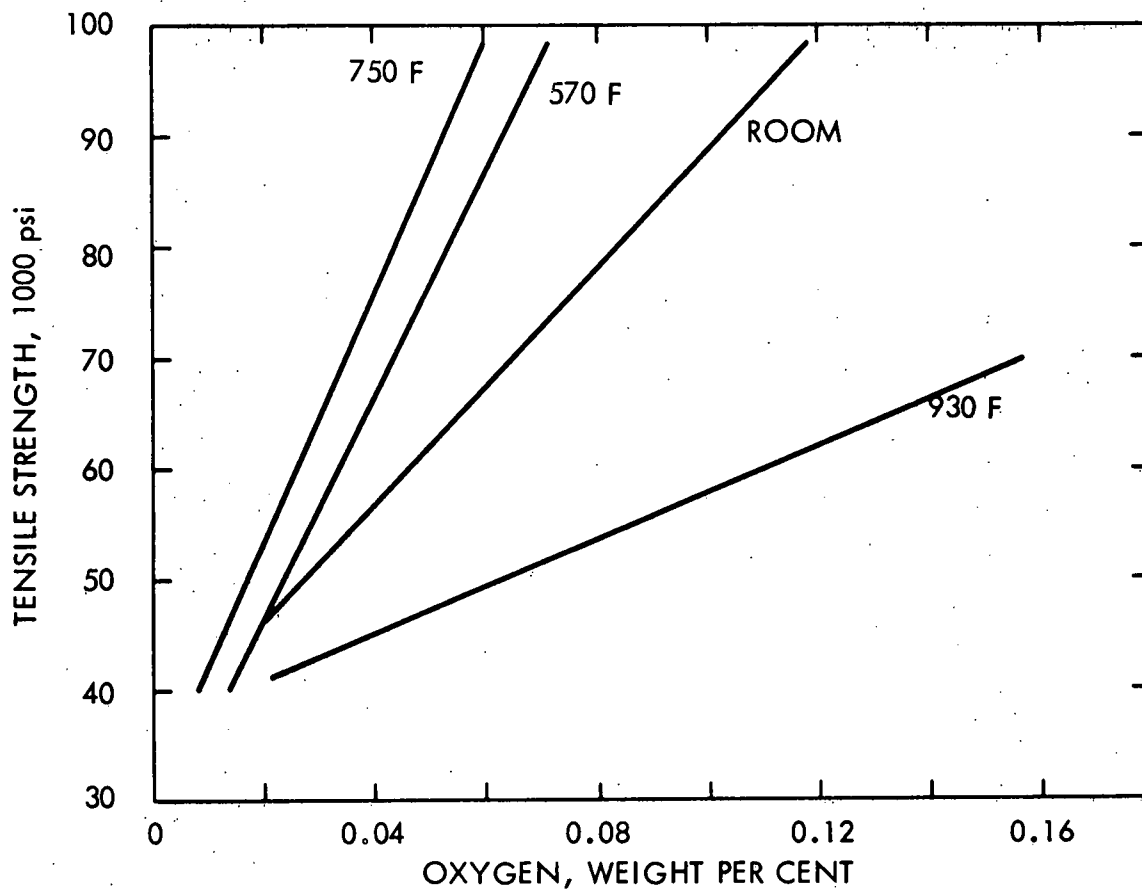


Figure 1. Effect of Oxygen on the Tensile Strength of Niobium at Various Temperatures (3)

TASKS	FY - 67												FY - 68						
	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	
<u>I. MELTING STUDIES</u>	_____																		
A. SCREENING EVALUATIONS	_____																		
B. SCALE - UP				_____															
C. COMMERCIAL PRACTICE						_____													
<u>II. FABRICATION AND MECHANICAL TESTING</u>								_____											
A. SHEET ROLLING							_____												
B. TENSILE TESTING								_____											
C. STRESS - RUPTURE TESTING								_____											
<u>III. WELDABILITY</u>								_____											
A. T. I. G. WELDING								_____											
B. ELECTRON BEAM WELDING								_____											
C. MECHANICAL TESTING												_____							

Figure 2. Vanadium Purification Work Program

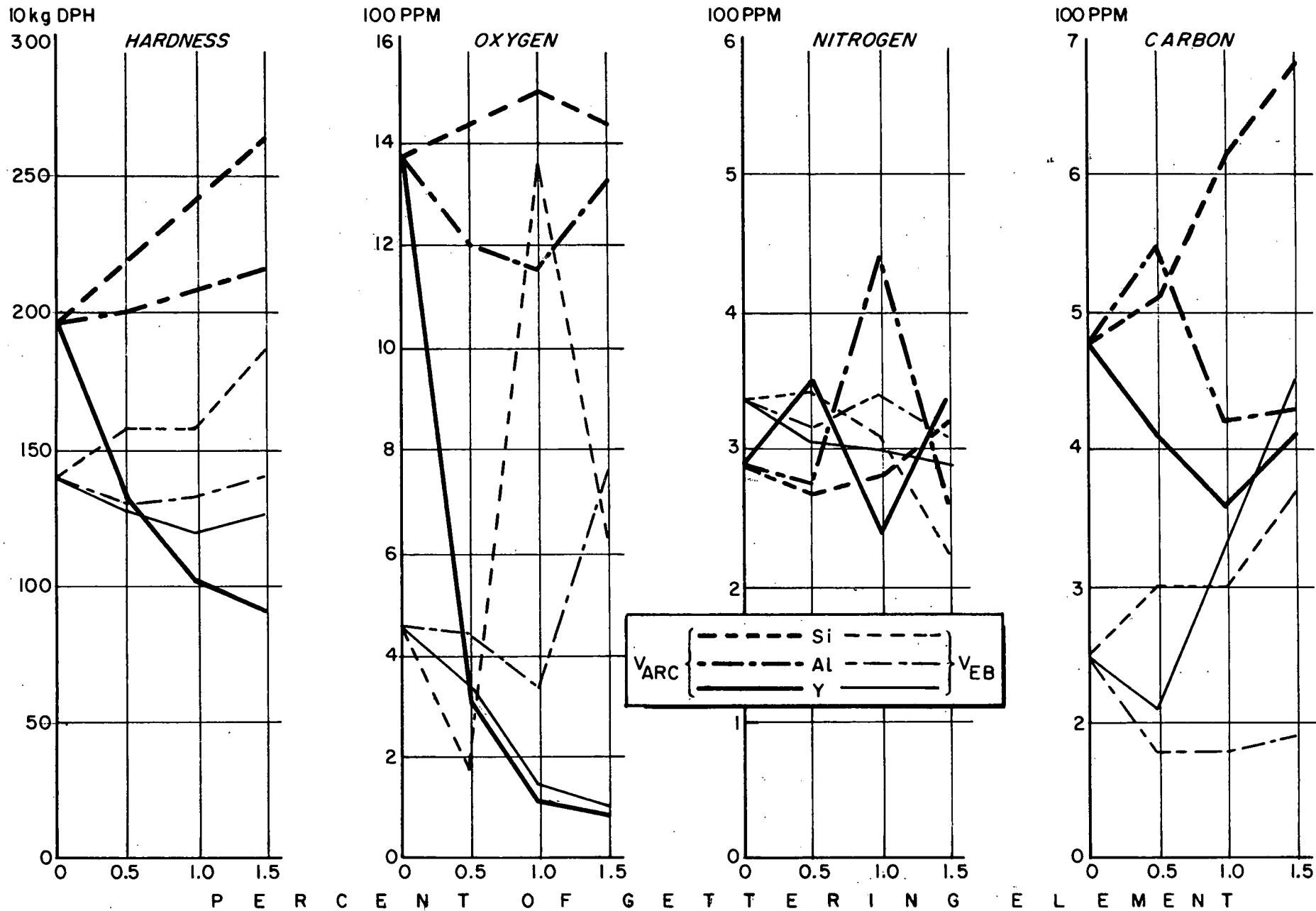
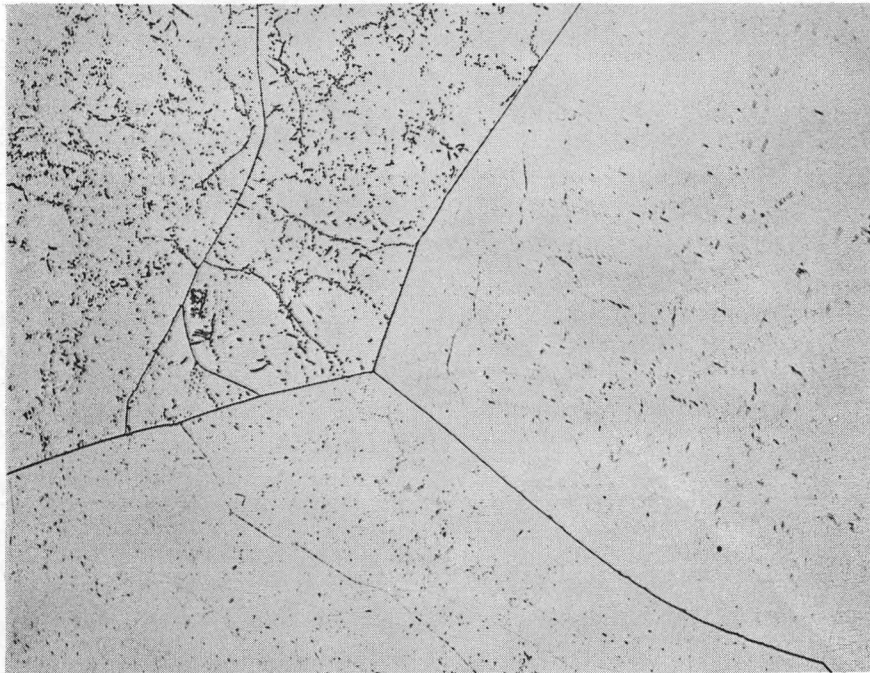
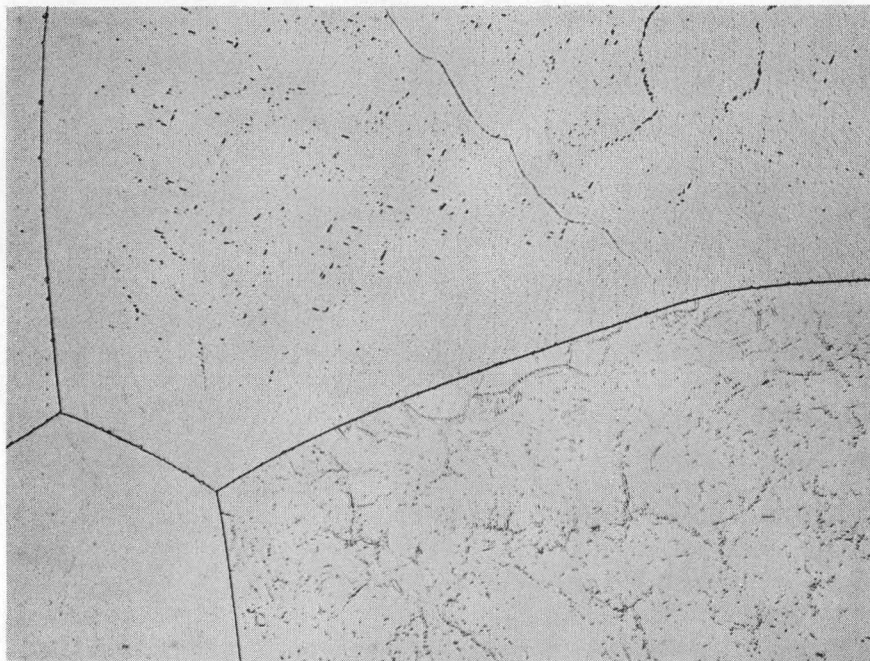


Figure 3. Effect of Gettering Element on Impurity Content



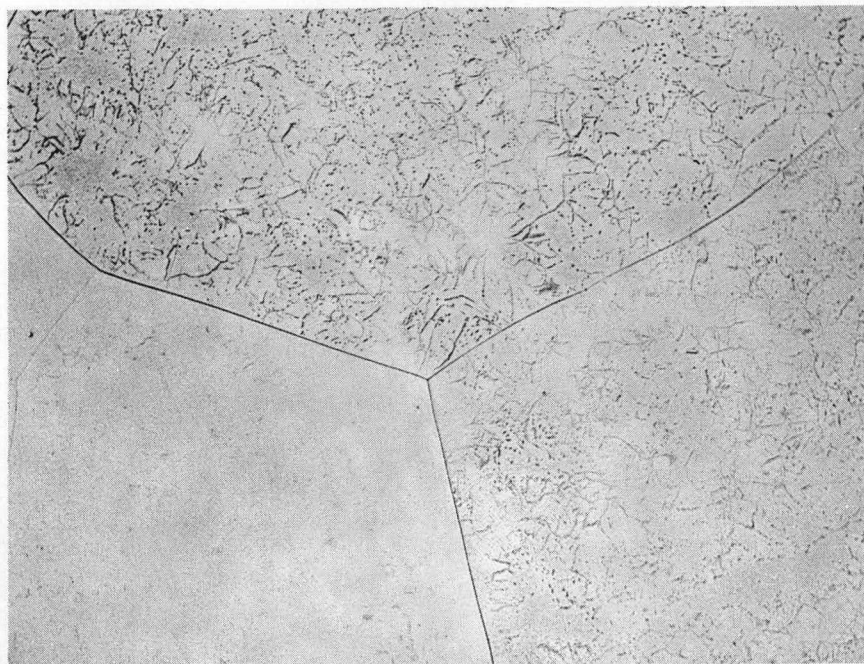
Mag. X250

Figure 4. Vanadium Granules After Arc Melting



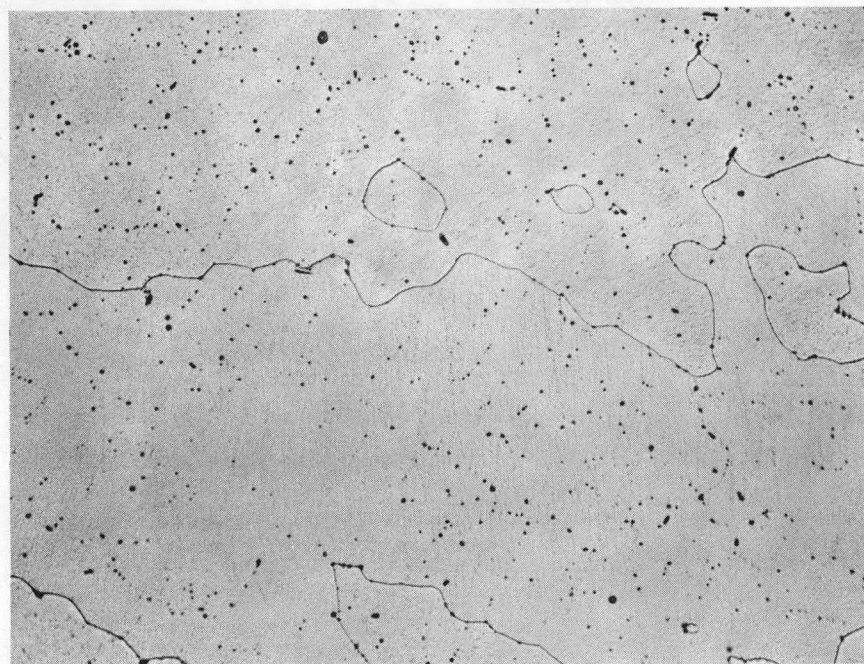
Mag. X250

Figure 5. Vanadium with 1.5% Aluminum After Arc Melting



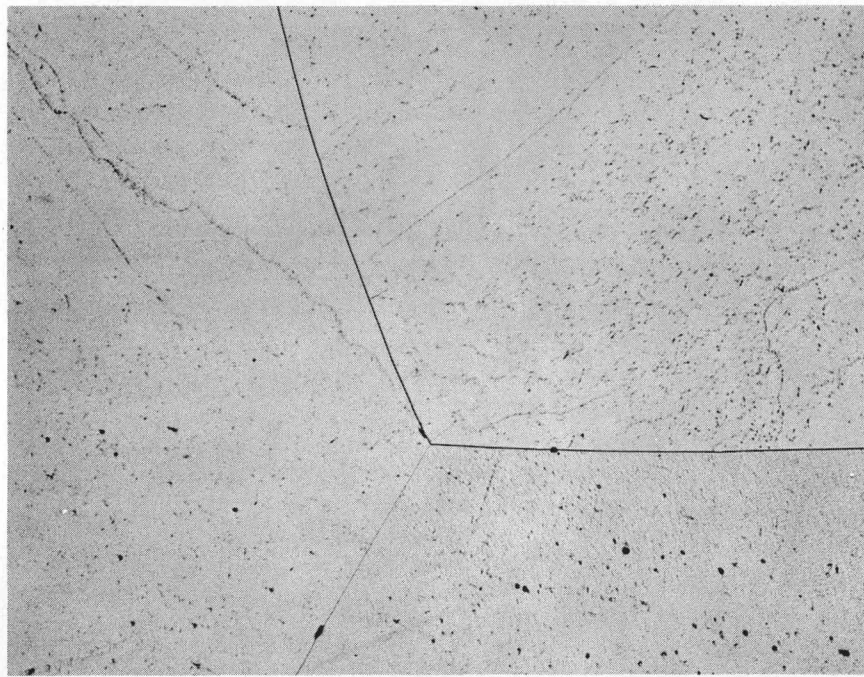
Mag. X250

Figure 6. Vanadium with 1.5% Silicon After Arc Melting



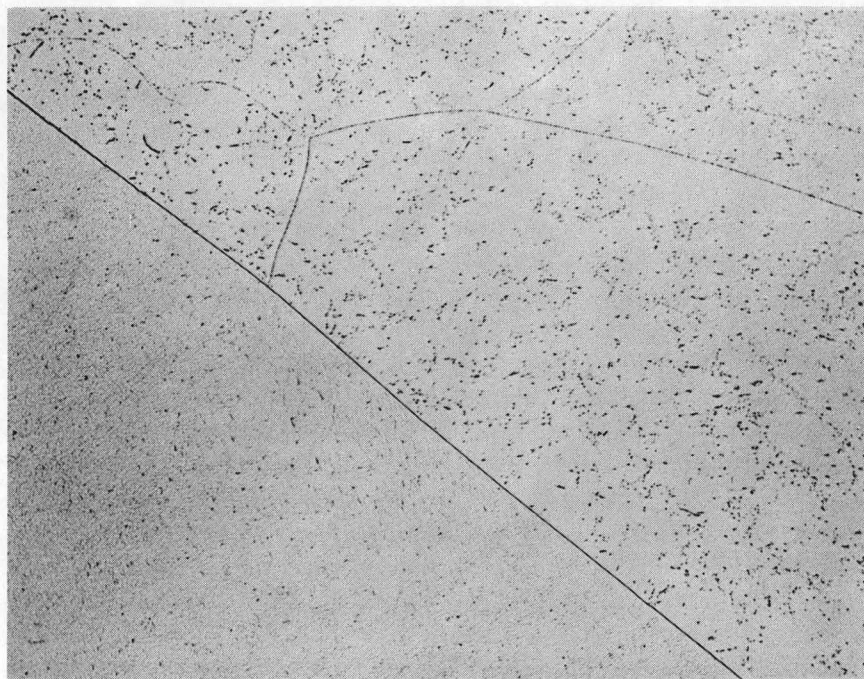
Mag. X250

Figure 7. Vanadium with 1.5% Yttrium After Arc Melting



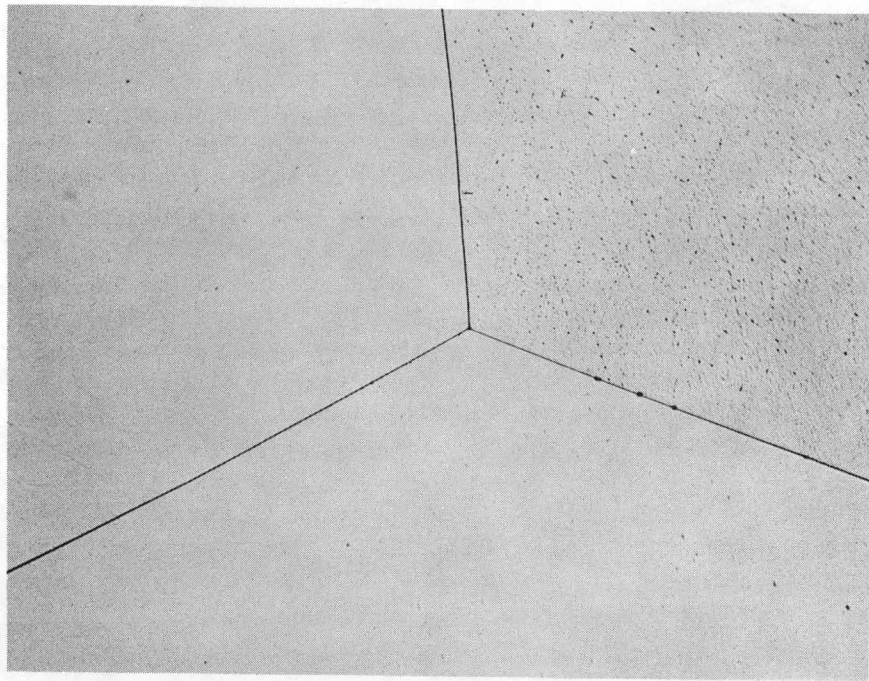
Mag. X250

Figure 8. Vanadium Granules After Arc Melting and E. B. Melting



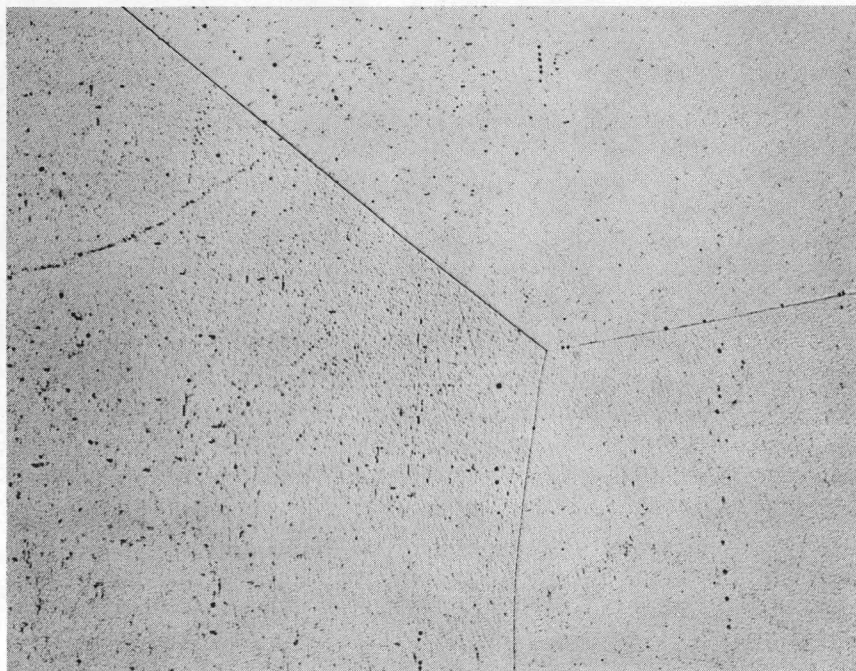
Mag. X250

Figure 9. Vanadium with 1.5% Aluminum After Arc Melting and E. B. Melting



Mag. X250

Figure 10. Vanadium with 1.5% Silicon After Arc Melting and E. B. Melting



Mag. X250

Figure 11. Vanadium with 1.5% Yttrium, After Arc Melting and E. B. Melting

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.