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MASTER

VANADIUM PURIFICATION

FIFTH QUARTERLY PROGRESS REPORT

Issued January, 1968

NUCLEAR POWER DEPARTMENT

COMBUSTION ENGINEERING, INC.

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CEND-3742-329
UC-25, Metals, Ceramics and Materials
TID-4500, 51st Edition

VANADIUM PURIFICATION
FIFTH QUARTERLY
PROGRESS REPORT

For Period
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VANADIUM PURIFICATION

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ABSTRACT

During this report period, 117 pounds of high purity vanadium were produced by a commercial process to meet the contract requirements. Additional material is being produced to demonstrate the repeatability of the process and to provide additional back-up material.

The process developed for the production of the high purity vanadium is as follows:

1. Aluminothermic reduction of V_2O_5
2. Consolidation by electron beam melting the reduced vanadium
3. Second electron beam melting
4. Yttrium vacuum-arc doping
5. Final electron beam melting.

II INTRODUCTION

This program was initiated to produce a 100 pound, high purity vanadium ingot by a process suitable for commercial applications. This material will be used as feedstock for producing a high purity, V-15 Cr-5 Ti, alloy ingot. Mechanical pro-perties of the alloy will be determined to evaluate the effect of purity on the tensile, stress rupture and weld characteristics of the alloy.

Prior to work performed during this quarter, two vanadium ingots were produced which did not fully meet the following target requirements of this program:

1. Weight

   Approximately 100 pounds

2. Chemistry

oxygen, nitrogen, carbon, hydrogen	$\leq$ 500 ppm
silicon	$\leq$ 500 ppm
aluminum	$\leq$ 1000 ppm
iron	$\leq$ 1000 ppm

3. Process

   By a reproducible, commercial process.

The first ingot produced was high in silicon and was contaminated by the reactant aluminum used for the aluminothermic reduction of V_2O_5.

The second ingot had a high initial oxygen content due to insufficient excess aluminum in the reduction process. Two extra electron beam melts were required and resulted in an ingot of insufficient weight.

Fabrication of the third ingot followed the outlined process and meets the requirements of the contract. Details of the processing of this third ingot are included in this report.

The fourth ingot is serving to demonstrate process reproducibility and to provide additional back-up material.

III EXPERIMENTAL EFFORT

During this quarter, 117 pounds of high purity vanadium (Ingot No. 3) were produced by the commercial process outlined in the Abstract of this report.

Aluminothermic reductions for the third ingot were processed and double electron beam melted during the last quarter. As reported in CEND-3742-325, seven derbies, totaling 342 pounds, were reduced with excess aluminum to allow residual aluminum in the reductions to aid in removing oxygen during electron beam melting. Table I gives the chemical analyses of the seven derbies.

During the consolidation of the derbies, the unmelted portion of the feedstock separated from the feedstock holding stub, causing a premature furnace shutdown. The melted portion, 139 pounds, was designated Heat Number 940014-V-X1A. The separated section was then melted into a 94 pound ingot, Heat Number 940017-V-X1A. The chemical and hardness data for both ingots are given in Table II.

The two consolidated ingots were welded together and used as the feedstock for the second electron beam melted ingot, 204 pounds, Heat Number 940020-V-53B. The chemical analyses and hardness data are shown in Table III. The section of the ingot which had a much higher hardness than the remainder was removed. This practice is typical of that used in commercial melting of columbium and zirconium ingots.

During this quarter, the balance of the ingot was vacuum-arc doped with yttrium, and final electron beam melted.

The doped ingot, designated Heat Number 6-950048-Y-Y weighed 147 pounds. The chemical and hardness data are shown in Table IV. The oxygen values noted, are not representative of the ingot because the oxygen content is not homogeneous, and is combined with the yttrium.

TABLE I

CHEMICAL ANALYSIS INGOT #3

Derby Analysis (ppm)

Derby No.	C	O	H	N	Si
8-7-67	80	1,300	50	70	600
8-8-67	50	1,400		45	400
8-9-67	140	3,900		115	400
8-10-67	90	10,100	47	144	300
8-11-67	120	14,400		230	300
8-24-67	150	1,400	34	200	270
8-25-67	100	4,360	31	400	260
Average	104	5,260	40	172	361

TABLE II

CHEMICAL ANALYSIS INGOT #3

Consolidation Ingot Analysis (ppm)

Heat No.	C	O	H	N	Si	Hardness, BHN 300 kg Load
940014-V-X1A						
Top	550	1,600	11	225	690	375
Center	500	--	--	95	610	156
Bottom	500	320	8	125	350	96
9400017-V-X1A						
Top	460	6,500	26	260	440	163
Center	470	1,000	3	125	440	192
Bottom	--	--	--	--	--	107
Average	496	2,355	11	166	506	181

TABLE III

CHEMICAL ANALYSIS INGOT #3

2nd Electron Beam Ingot Analysis (ppm)

Heat No.	C	O*	H	N	Si	Hardness, BHN 300 kg Load
940020-V-53B						
Top 1	60	640	9	135	420	96
2	60			305	350	254
3	50	360	9	350	460	96
4	50			120	610	180
Bottom 5	100	440	6	250	870	165
Average	64	480	8	232	542	158

TABLE IV

ARC DOPED INGOT ANALYSIS (ppm)

Heat No.	C	O*	H	N	Si	Hardness, BHN 300 kg Load
6-950048-VY						
Top 1	60	610	--	175	440	69
2	50		--	185	570	74
3	60	1,060	--	185	700	77
4	50		--	160	560	71
Bottom 5	50	730	--	175	360	86
Average	54	800	--	176	526	75

*The oxygen values are not representative because the oxygen is tied up with yttrium.

During the final electron beam melting of the ingot, a malfunction of the molten pool-height control ram caused the molten vanadium to overflow the crucible, causing a premature shutdown. The portion melted was designated Heat Number 940021-V-52A. The remaining portion was melted into a separate ingot, Heat Number 940022-V-52A. Table V indicates the hardness and chemical data of the final ingots and shows that the ingots meet the requirements of the contract.

A fourth ingot has been started during this quarter. Three batches of high purity V_2O_5 from two sources, Vanadium Corporation of America and Kerr McGee, have been aluminothermically reduced. While the quantity of metal produced in these three reductions, 150 pounds, is not adequate to produce a full 100 pound ingot (a yield of 60 pounds is expected). Sufficient V_2O_5 of suitable purity was not available to produce a larger quantity. Material already procured at Wah Chang, had too high a silicon content. Wah Chang is discussing the situation with the two suppliers of V_2O_5.

The furnace used in the reduction of the three derbies for the fourth ingot was slightly modified to decrease possible contamination of the material during the reduction process. Past experience has shown that a moderator was necessary to retard the rate of the aluminothermic reaction. Too violent a reaction caused excessive splattering and contamination. The furnace was modified by installing an Al_2O_3-lined steel lid over the reaction zone inside the furnace. This acts as a shield, reducing splattering and eliminating the need for an Al_2O_3 moderator. This further reduces the possibility of silicon contamination from the Al_2O_3.

Past experience has also shown that excess amounts of aluminum in the derbies (reductions) aid in the subsequent removal of oxygen during electron beam melting.

TABLE V

CHEMICAL ANALYSIS INGOT #3

Final Electron Beam Ingot Analysis (ppm)

Heat No.	C	O	H	N	Si	Hardness, BHN 3,000 kg
940021-V-52A						
Top 1	110	360	5	199	610	116
2	90					143
Bottom 3	70	200	5	197	550	121
940022-V-52A						
Top 1	130	210	5	199	520	137
2	80					116
Bottom 3	90	260	5	197	570	131
Average	95	260	5	198	562	127

TOTAL = 558 ppm interstitials

TABLE VI

CHEMICAL ANALYSIS INGOT #4

Derby Analysis (ppm)

Derby No.	C	O	H	N	Si
11-13-67	220	4,390	--	45	210
11-17-67	115	2,600	--	65	100
11-27-67	170	3,060	--	125	400
Average	168	3,350	--	78	240

Therefore, for the fourth ingot, a substantial amount (15%) of excess aluminum was used to lower the oxygen content. Chemical analyses of the three derbies are shown in Table VI.

Two consolidation ingots were melted, one containing derbies 11-13-67 and 11-17-67, with 11-27-67 being melted separately since the silicon level of this material was marginal. Separation of the materials would not be necessary in a production operation provided a sufficiently pure pentoxide was available. Chemical and hardness data of the consolidation ingots are shown in Table VII.

The two ingots were second electron beam melted and designated Heat Number 940027-V-54B. The chemical and hardness data are shown in Table VIII.

TABLE VII

CHEMICAL ANALYSIS INGOT #4

Consolidation Ingot Analysis (ppm)

Heat No.	C	O	H	N	Si	Hardness, BHN 3,000 kg
940023-V-54A	370	420	3	180	380	217
(Derby 11-27-67)	290	290	9	170	270	181
940026-V-54A	270	440	4	110	390	86
(Derbies 11-13-67	230			100	310	109
11-17-67)	310	200	5	90	300	116
Average	290	340	5	130	330	142

TABLE VIII

CHEMICAL ANALYSIS INGOT #4

Second Electron Beam Ingot Analysis (ppm)

Heat No.	C	O	H	N	Si	Hardness, BHN
940027-V-54B	200	160	3	90	300	99
	140	170	--	100	390	96
	130	130	--	210	370	187
	140	430	8	200	480	170
Average	150	220	6	150	390	138

TOTAL = 526 ppm Interstitials

IV DISCUSSION OF RESULTS

The chemical analyses for the third ingot, shown below, indicate that the chemical requirements for the contract have been met.

Element	Target Value (ppm)	Contract Requirement (ppm)	Average Ingot Analysis (ppm)	
Oxygen	300	≤ 500 (O, N, C, H combined)	260	558 (O, N, C, H combined)
Nitrogen	100		198	
Carbon	100		95	
Hydrogen	10		5	
Silicon	500	≤ 500	562	
Aluminum	1000	≤ 1000	<100	
Iron	1000	≤ 1000	204	

The variation in the interstitial and silicon contents (11 and 12% respectively), from the contract requirements, are within the accuracy of analyzing for these elements.*

*Verbal communication, Bureau of Mines, Albany, Oregon.

The effects of vacuum melting on the hardness and chemistry of Ingot Nos. 2, 3 and 4 are shown in Figures 1 through 5.

Figure 1 shows the decreasing hardness of the ingots during purification. The reasons for the variation in hardness between the ingots are not obvious based upon the effects of individual constituents. It is suspected that the as-cast hardness is not the dead soft condition and therefore, cannot be taken as an effective measure of impurity levels. This was suggested by Rostoker and Hansen (Ref: Wright Air Force Development Center Technical Report 52-145, Part I, 1952) on cast buttons. In that investigation, molybdenum, beryllium and titanium all caused increases in the as-cast hardness, which could be subsequently lowered by annealing. It is likely that the interstitials and aluminum could behave similarly in vanadium.

It is also possible that the ingots are not totally homogeneous at this stage. A variation in grain size is noted along the length of the ingot. The size appears to vary inversely with the hardness. Sampling within these areas will be performed to detect the chemical variance.

The curves show decreasing hardness after each electron beam melt, with a slight increase after arc doping.

Figure 2, shows the effect of residual aluminum upon the rate of oxygen removal during electron beam melting. The greater residual aluminum content in the derbies for Ingot No. 3 (1.92 wt/o Al) and No. 4 (15.4 wt/o Al) versus Ingot No. 2 (0.92 wt/o Al) greatly increases the rate of oxygen removal. Whereas previously, oxygen was removed during electron beam melting by the $C + O_2 \rightarrow CO_2$ process, it is removed now primarily by combining with the aluminum. Earlier in

FIG. 1: EFFECT OF VACUUM MELTING ON THE HARDNESS READING OF VANADIUM

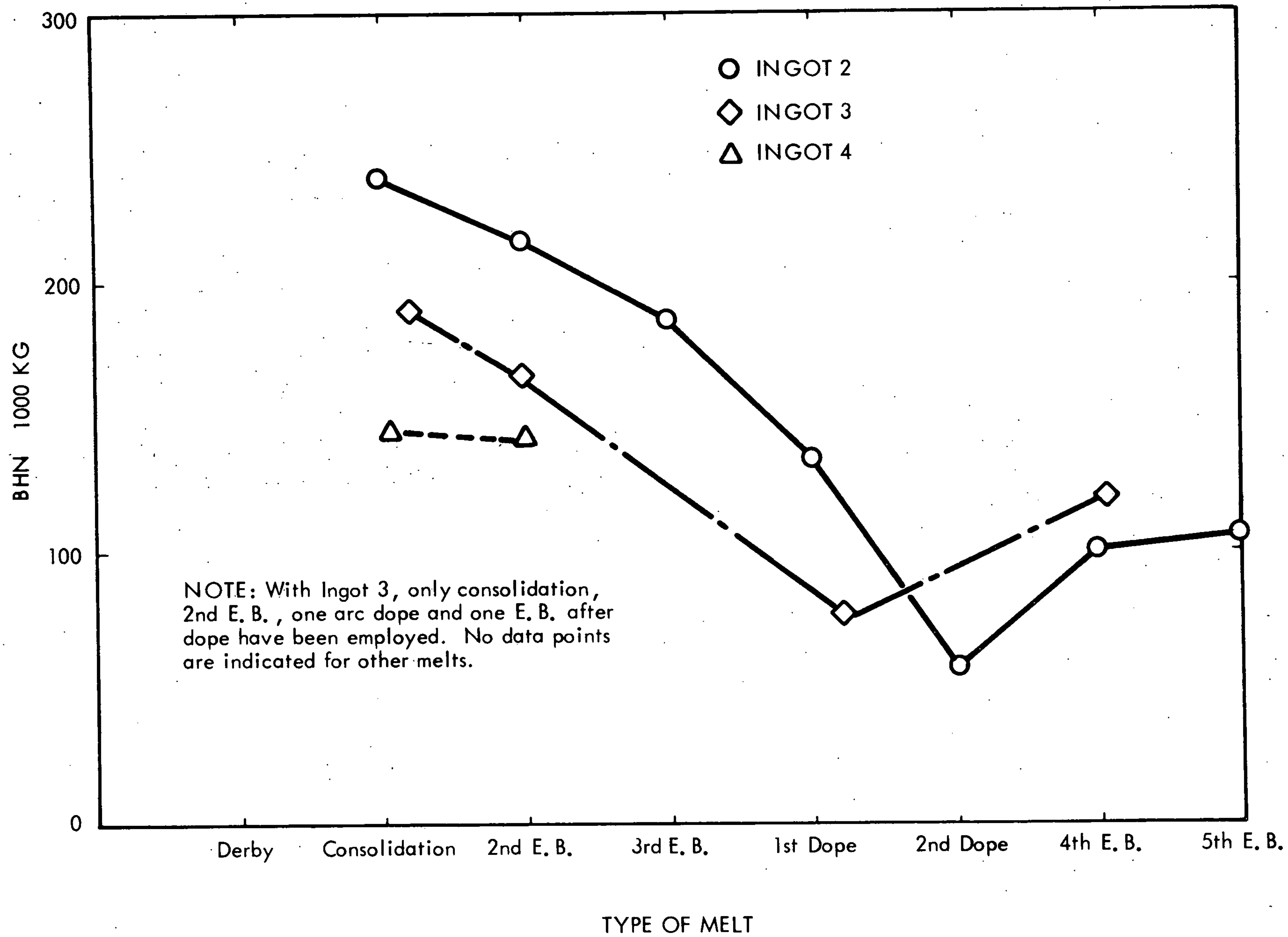
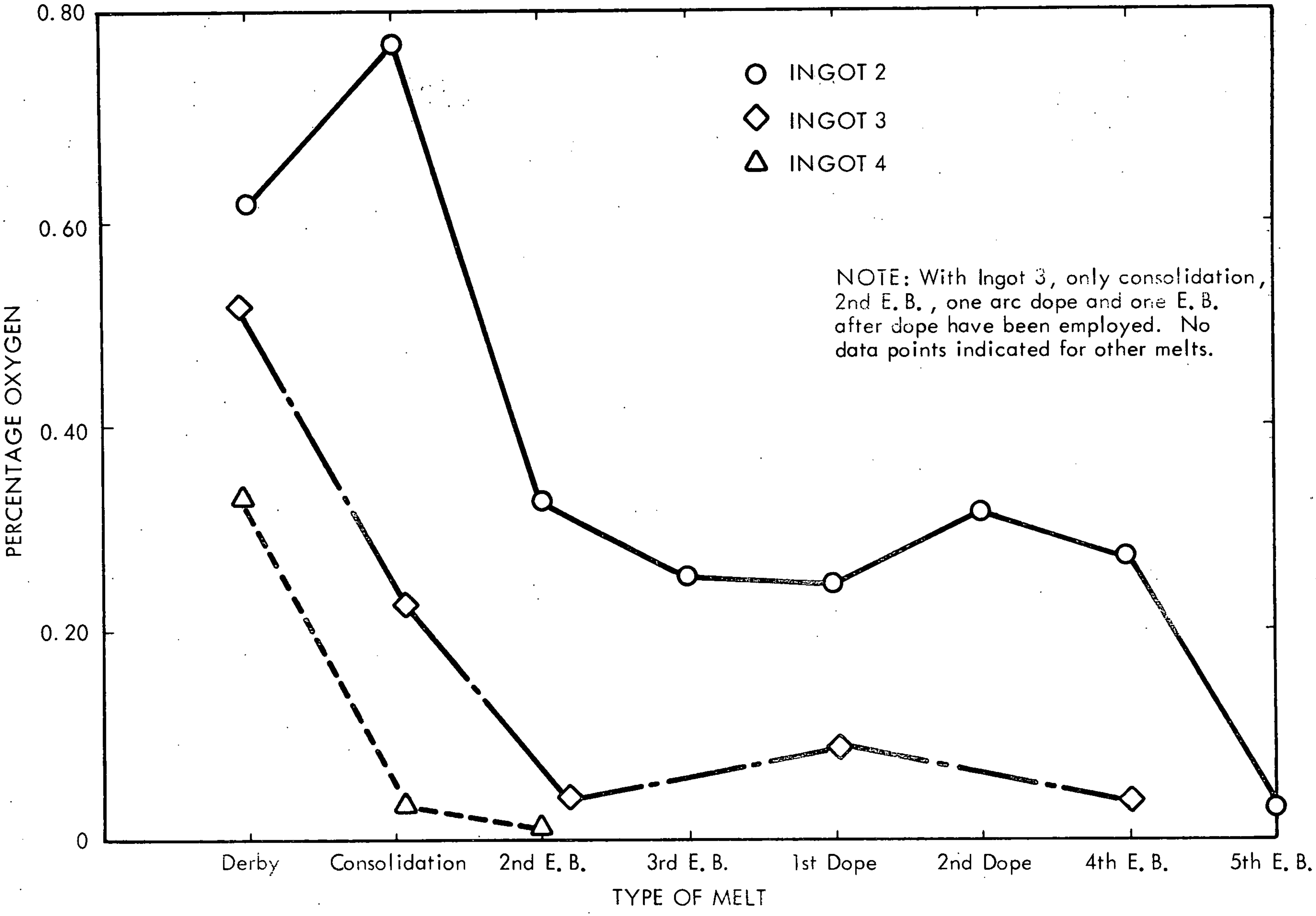


FIG. 2: EFFECT OF VACUUM MELTING ON THE OXYGEN CONTENT IN VANADIUM



the program, it was felt that an excess of aluminum would lead to serious problems in electron beam melting, since arcing problems had been encountered in the melting of high aluminum, columbium thermite reductions. However, these problems were not encountered.

Figure 3 shows some inconsistancies which are probably a result of sampling errors and the heterogenious nature of the derbies and consolidation melt material. However, the data indicate that the carbon is not removed as rapidly when excess aluminum is retained in the derbies. Possibly, the excess aluminum reacts with the oxygen and reduces the oxygen available to react with the carbon.

Figure 4 shows that the nitrogen level can double during the complete process. It became obvious that nitrogen cannot be removed by vacuum melting, consequently, every effort must be made to avoid nitrogen contamination during all processing.

Figure 5 shows that, neglecting inaccurate derby analyses, the silicon level remains essentially constant through the ingot production.

It is apparent that one of the major limitations in producing high purity vanadium metal is the quality of V_2O_5 available. This is especially true with respect to silicon content since the two elements are so similar chemically and would be expected to behave similarly in thermite and electron beam operations.

The chemical analyses of the fourth ingot after the second electron beam melt, show that the ingot, 77 pounds, already meets the chemical requirements without doping. The excess residual aluminum eliminates the doping step, further enhancing the process for commercial application.

FIG. 3: EFFECT OF VACUUM MELTING ON THE CARBON CONTENT IN VANADIUM

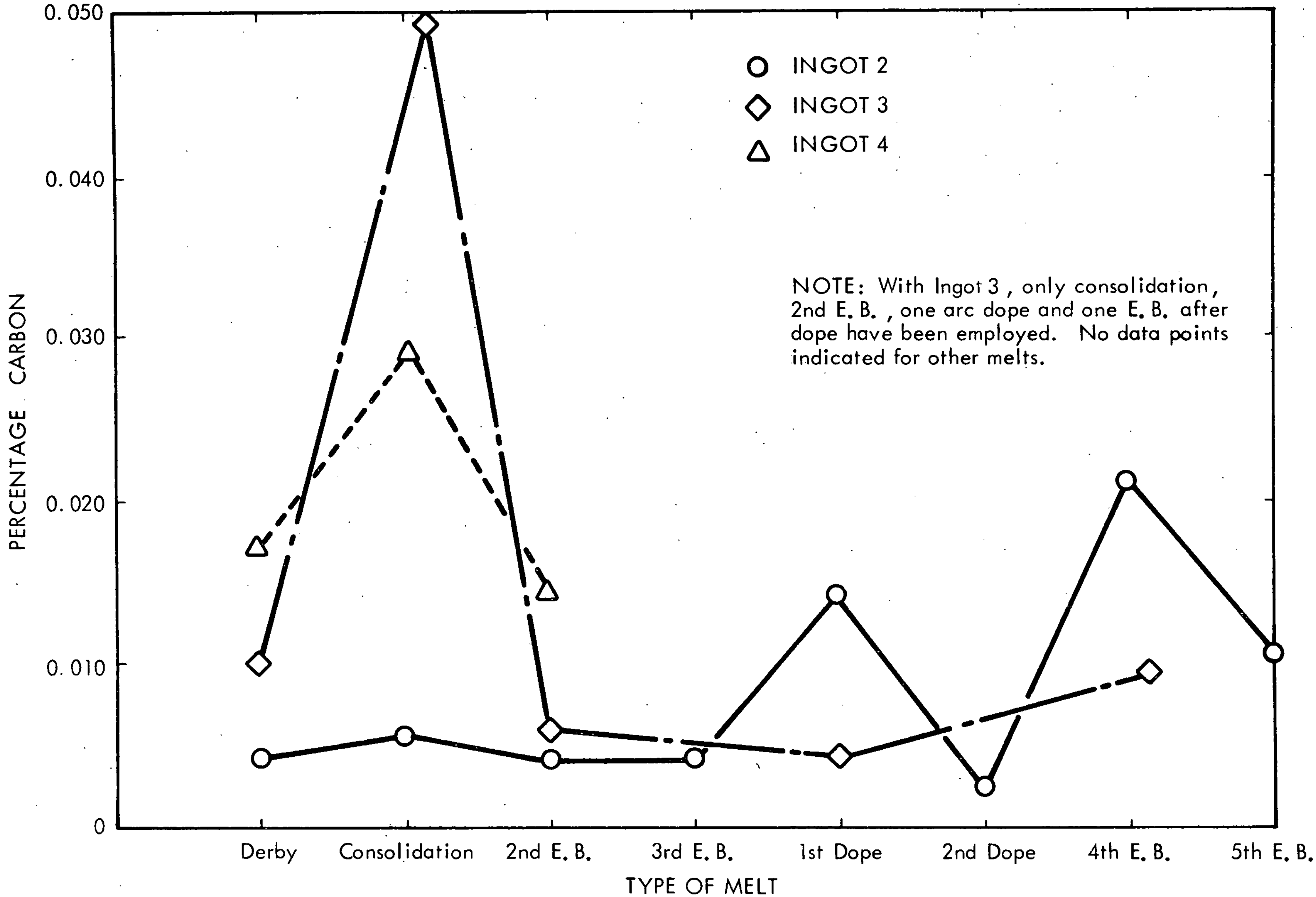


FIG. 4: EFFECT OF VACUUM MELTING ON THE NITROGEN CONTENT IN VANADIUM

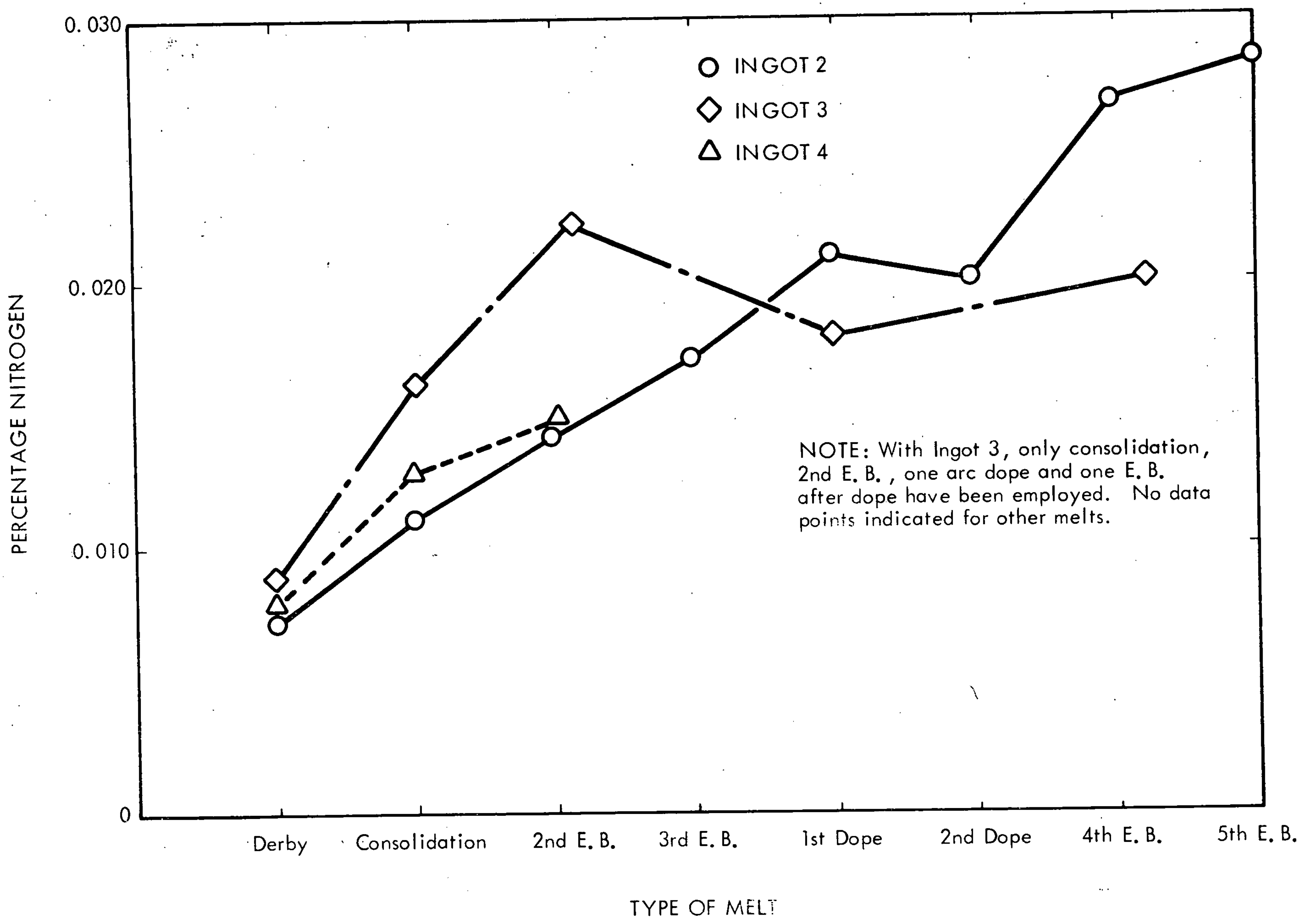
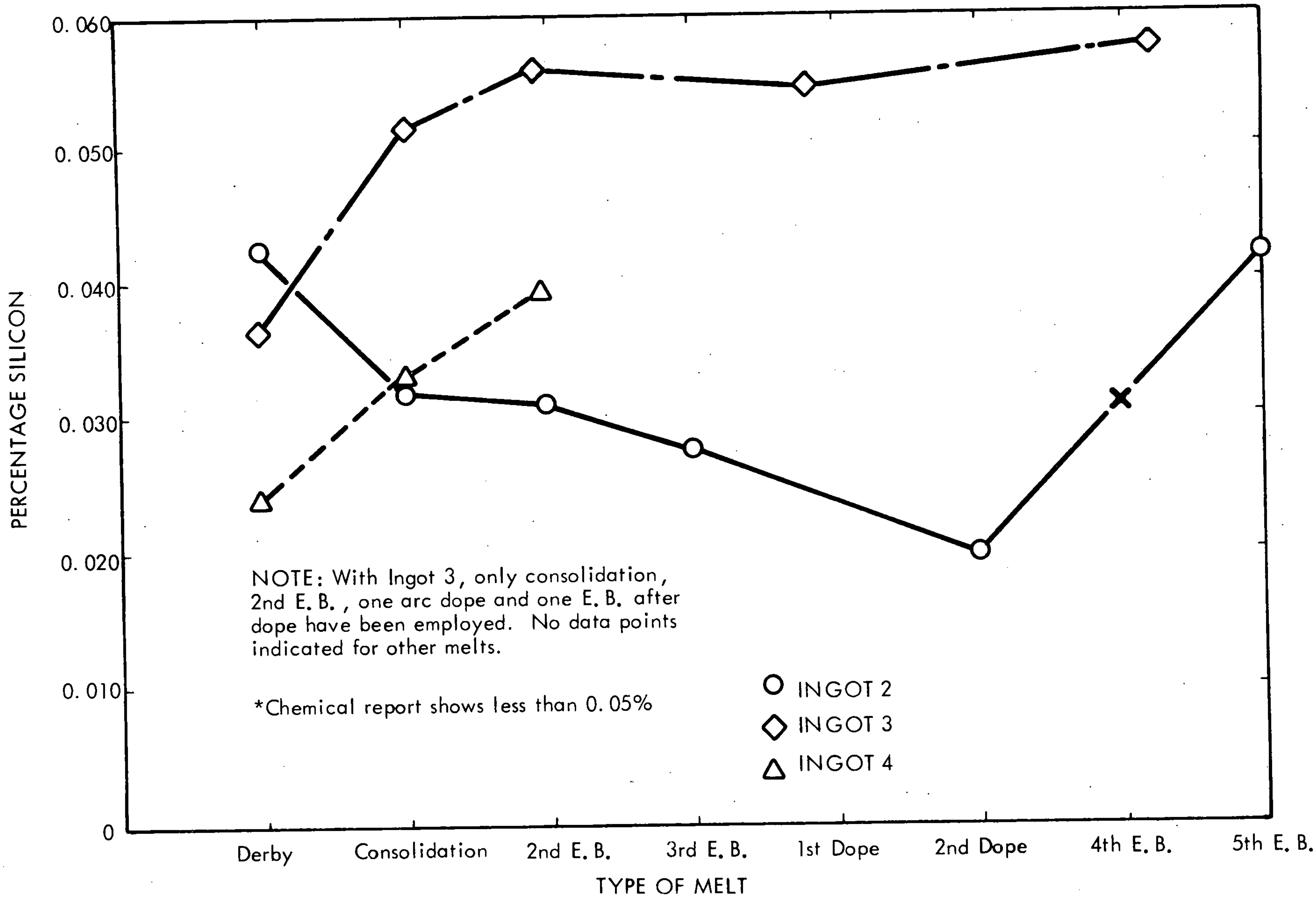


FIG. 5: EFFECT OF VACUUM MELTING ON THE SILICON CONTENT IN VANADIUM



V FUTURE WORK

When ingots 3 and 4 are accepted as satsifying contract requirements, the ingots shall be blended, as in the commercial processing of columbium and titanium, and processed into a single ingot of approximately 200 pounds. 100 pounds of this shall be used to produce a high purity V-15 Cr-5 Ti alloy.