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2021-07-30

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Original Publication Citation

Rappleye, D., & Haun, R. (2021). Production of Pure Vanadium: Industry Review and Feasibility Study of Electron Beam Melt Refining of V–Al Alloys. *Journal of Sustainable Metallurgy*, 7(3), 755–766. <https://doi.org/10.1007/s40831-021-00407-6>

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Rappleye, Devin and Haun, Rob, "Production of Pure Vanadium: Industry Review and Feasibility Study of Electron Beam Melt Refining of V–Al Alloys" (2021). *Faculty Publications*. 5899. <https://scholarsarchive.byu.edu/facpub/5899>

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Production of Pure Vanadium: Industry Review and Feasibility Study of Electron Beam Melt Refining of V-Al Alloys

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Keywords: Vanadium, Electron Beam Melting, Master alloys

Abstract

The vanadium industry has experienced significant change over the last two decades with the emergence of vanadium redox flow batteries for grid-level energy storage, the growing demand for high-strength steel, and the selection of vanadium as a critical material in multiple countries. This review presents the status of the vanadium industry examining production processes and detailing facilities. The available information for each producer is presented including vanadium products and capacity. The production of pure vanadium is identified as a potential vulnerability for some nations where vanadium metal is needed in small, yet strategic, applications and globally only two producers of pure V were identified. One potential method to produce pure V is electron beam melt refining. Exploratory electron beam melt refining trials were performed on kilogram quantities of master (V-Al) alloys from the aerospace industry to explore the use of commercially available vanadium alloys to produce pure vanadium metal with minimal processing, as a means to mitigate potential risks.

Introduction

A review of the vanadium production processes and industry was published in 2003 [1]. However, much has changed in the vanadium industry due to regulations increasing the demand for high-strength steel [2–4], the emergence of vanadium redox flow batteries (VRFB) as a strong competitor in grid-level energy storage [5–7], and the identification of vanadium as a critical material by multiple nations [8–11]. A recent review thoroughly covered the processing and sourcing of vanadium minerals with a focus on technological developments towards sustainability [12]. Our review seeks to provide a brief overview of the processing of vanadium

minerals to various products, the producers of various vanadium products and to evaluate gaps and vulnerabilities in the industry.

As a result of the review of the vanadium industry, the supply of pure vanadium was identified as a vulnerability in the industry. In some countries, pure vanadium is needed in small, yet strategic applications, like the manufacturing of infrared cameras, cladding titanium to steel for airframe joints, and other applications [13]. Yet, these countries do not have the purification of vanadium integrated into their industry due to their small and inconsistent demand. Therefore, the ability to produce pure vanadium from commercially available vanadium compounds to pure vanadium in a single processing step would be valuable to such countries.

Electron beam melt (EBM) refining can potentially produce pure vanadium from a commercially available master alloy in a single processing step. Electron beam melting is implemented to refine silicon, refractory metals, titanium alloys, and other metals and alloys [14–18]. EBM refining is accomplished by melting a metal via an electron beam under high vacuum. The more volatile components evaporate preferentially, purifying the higher melting point metals (e.g., tungsten, niobium, and tantalum). Some countries previously employed and a couple still employ electron beam melting for purifying vanadium as part of a fully integrated process [1, 14, 19]. EBM furnaces could potentially be used by some countries to close the gap to pure V by purifying commercially available vanadium alloys and/or upgrading their scrap.

Review of Vanadium Industry

Vanadium Processing and Products

The generalized flowsheet from minerals to the various vanadium products is displayed in Figure 1 which is adapted from various sources [19–22], where historical and current processes are described in greater detail. The vanadium sources being used by most of the current producers are listed on the left. The approximate percentages below the process flow lines indicate the estimated fraction of vanadium that is produced from the respective source(s) [23, 24]. Often vanadium is produced as co-product or secondary product. Hence, if the source material undergoes processing for a different product, then the byproduct from the process that contains concentrated vanadium is listed as a V-bearing byproduct. The major processing steps by which vanadium is extracted from the source or byproduct are displayed in the center column of Figure 1. The figure does not intend to capture all the processing routes employed or investigated in the literature. Almost all commercial processes precipitate V_2O_5 as either the final or intermediate product. The percentages listed in each product box indicates the fraction of vanadium that flows into that product. It should be noted that V-salts is the place holder for all vanadium chemical products (e.g., V_2O_5 , $VOSO_4$, VCl_4) of which V_2O_5 comprises the great majority. If V_2O_5 or another vanadium chemical is not the final product, then it undergoes a pyrometallurgical reduction process. Most ferrovanadium (FeV) manufacturers use the aluminothermic reduction process. If creating FeV, then a desired amount of iron is mixed with vanadium during the

reduction process to achieve a certain V grade. When a master alloy (VAI) is being made, only aluminum is added, but in varying degrees of excess to achieve a desired V grade. EBM refining is required after the aluminothermic reduction to produce pure vanadium (>98.3 wt. %) by distilling the remaining aluminum and other impurities (e.g., Fe, C, O) from the alloy.

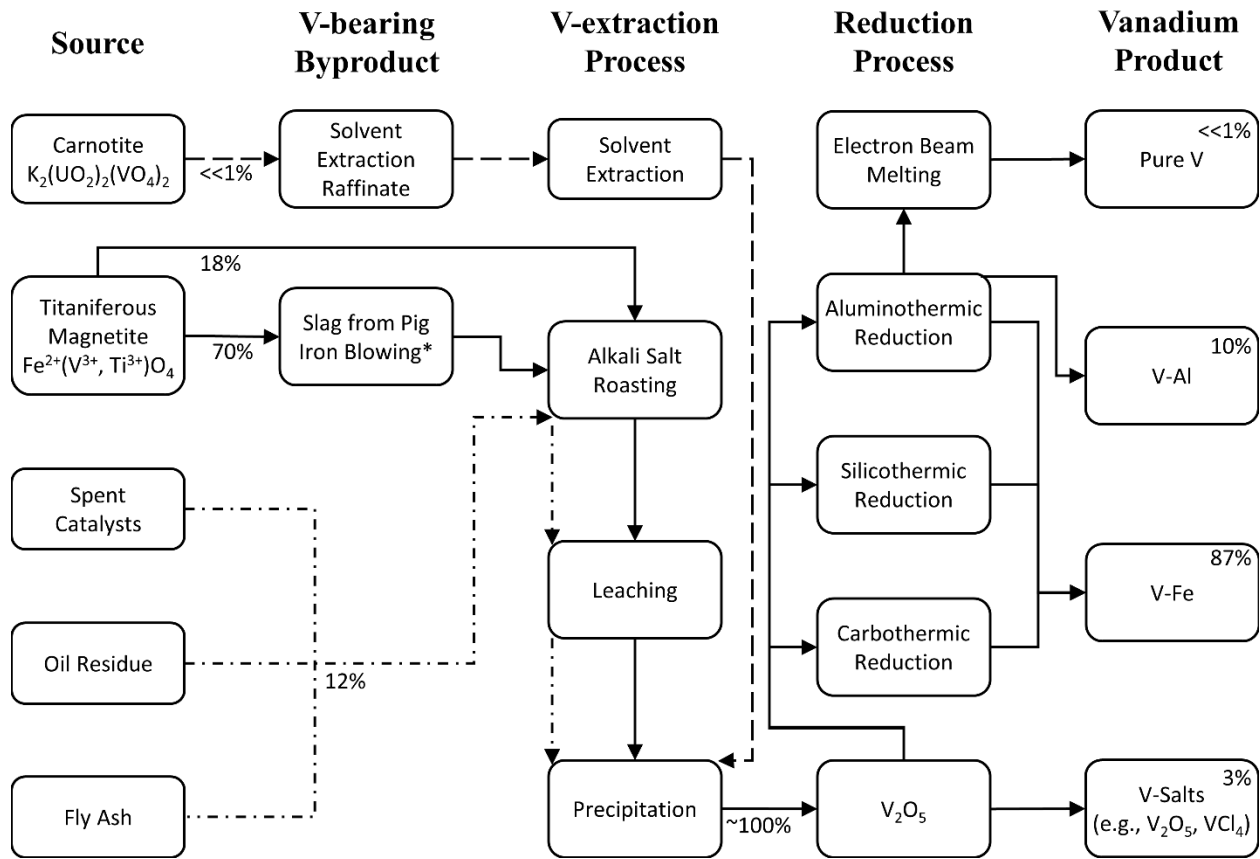


Figure 1. Generalized flow diagram for the major sources of vanadium to the main products. Percentages from [23, 24] (*includes stockpiled slag).

The overwhelming majority (~88%) of vanadium is produced from vanadiferous titanomagnetite (VTM), also called titanomagnetite or titaniferous magnetite. VTM is a deposit of magnetite (Fe_3O_4) in which the trivalent (i.e. ferric) iron is occasionally substituted with trivalent vanadium or trivalent titanium. The grade of vanadium in commercially viable VTM deposits is 0.2-1.6 wt. % V_2O_5 [25–27]. Nearly 80% of the VTM extracted is primarily processed to produce iron for steelmaking and vanadium is produced as a secondary product. In general, the VTM is reduced with coal or coke in a blast furnace or an electric furnace with prereduction in a rotary kiln to produce pig iron which contains most of the vanadium. The molten pig iron is refined with oxygen to remove vanadium into a $FeO \cdot V_2O_3$ slag (10-25% on V_2O_5 basis). The vanadium-rich slag also contains common components of slag, like CaO , MgO , Al_2O_3 , and possibly TiO_2 [19].

The vanadium slag undergoes a few minor processing steps (crushing, milling, magnetic separation) to yield a concentrate. The number and type of these steps vary between facilities, but the majority perform an alkali-salt roasting or acid leaching to concentrate the vanadium. Sodium salt (NaCl, Na₂CO₃, Na₂SO₄, etc.) roasting is commonly used and oxidizes the magnetite to hematite (Fe₂O₃) and forms sodium vanadate (NaVO₃) from the oxides (V₂O₃, V₂O₅). The conversion creates a water-soluble compound of vanadium which enables the next step of leaching. During leaching soluble sodium vanadate is dissolved and the iron oxides and other insoluble impurities form a “cake” in the leaching residues. The residues are removed, the sodium vanadate solution is transferred and sometimes filtered before the precipitation process. The vanadium is precipitated by the addition of ammonium salts (e.g. NH₄SO₄, NH₄Cl) and sulfuric acid (or hydrochloric acid). This forms sparingly-soluble ammonium metavanadate (AMV), NH₄VO₃ [28, 29]. The precipitated AMV is heated to be dried, then decomposed into V₂O₅, ammonia, and water. The V₂O₅ is often melted and formed into flakes. If VTM is being processed primarily for vanadium, then the ore typically undergoes the salt roasting process without the initial steelmaking processes in the previous paragraph [23, 27].

The processing of spent catalysts, oil residues and fly ash typically follows the process of roast, leach and precipitate similar to VTM ore extraction with additional steps of filtering and some additional processing (solvent extraction, ion exchange) of waste streams [12, 19, 21, 22]. Common metals that are also present in spent catalysts with vanadium are Mo, Ni, Co, and Al [21, 22].

Finally, the amount of vanadium produced from carnotite is insignificant in comparison to other sources. Energy Fuels Inc. near Blanding, Utah is the only known, active producer of vanadium that utilizes carnotite ore as a source. For a detailed description of processing of carnotite to extract uranium and vanadium, an extensive report has been published [30]. Initially, the ore is leached with sulfuric acid to extract the U and V. The pregnant leach solution is washed, thickened, and clarified before undergoing solvent extraction. The raffinate from solvent extraction is vanadium-rich. The raffinate is stripped of vanadium using soda ash, then precipitated to form AMV. The AMV is heated and dried to remove ammonia and water and form vanadium oxide. The oxide is melted, then cooled on casting wheels to form flakes. Some aspects of this process have recently changed to improve the purity of V₂O₅ to meet the demands of VRFB manufactures [31].

Many types of vanadium alloys are available including, but not limited to, FeV, VAl, VN, FeNV and FeMoV [19]. FeV and VAl are the most common alloys. FeV, VAl and pure V are produced almost exclusively by aluminothermic reduction of V₂O₅. This is performed inside a water-cooled copper crucible or a refractory lined crucible. Ideally, the reduction is performed under vacuum, in an inert atmosphere or under a flux to avoid nitrogen pickup, which is difficult to remove and cannot be removed via electron beam melting. An excess of 11-19% aluminum must be used to avoid excessive oxygen contamination. For example, at a stoichiometric equivalent amount of Al, a residual oxygen content of 1.7% is present in the produced V metal. At 15%

excess of Al, the residual oxygen is reduced to 0.24% [14]. The alloys of FeV and VAl are produced by performing the aluminothermic reduction with iron or excess aluminum. If pure V is desired, then electron beam melt refining is required.

Electron Beam Melt Refining

Due to vanadium's high melting point and low vapor pressure, many impurities can be removed by melting the metal under high vacuum. As shown in Figure 2, the vapor pressure of vanadium is lower than most metallic impurities. Aluminum and most transition metals can be removed by evaporation while melting the metal under vacuum. Refractory metals, like molybdenum, tungsten and tantalum cannot be removed. Nitrogen and carbon can also be problematic due to the formation of nitrides and carbides with high melting points. These impurities will increase in concentration due to the loss of other impurities and some vanadium. Oxygen can be removed due to the formation of aluminum suboxides and vanadium oxides in the low oxygen environment which have high vapor pressure [32–34]. Many of the details on the processing and refining of vanadium metal were found and are discussed in greater details by Gupta [14].

The evaporation rate will be a major factor in the purity of vanadium achievable. An estimation of the evaporation flux (J) in an electron beam furnace can be calculated using the Hertz-Knudsen equation [35, 36]:

$$J = \frac{p^o}{\sqrt{2\pi MRT}} \quad (1)$$

where p^o is the vapor pressure, M is the molecular weight, R is the universal gas constant, T is the temperature in K. The vapor pressures and the calculated flux from equation (1) are plotted in Figure 2 and in Figure 3, respectively. Aluminum can be removed to a low level, even with high initial concentrations, because of its high evaporation rate. Interestingly, the evaporation curve for Si, the element closest in vapor pressure to V, becomes closer to the V curve, especially at higher temperature, due to the large difference in molecular weights. These calculations assume ideal behavior (i.e., no interaction in liquid or gas phases). Despite this assumption, the calculations provide a good initial expectation of evaporation rates because pure species vapor pressure has been reported to have a greater effect on evaporation rates than activity coefficients in V-Al-Ti alloys [35].

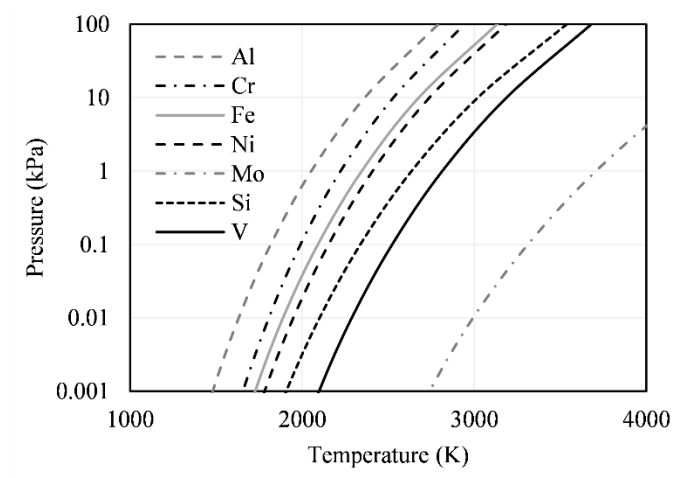


Figure 2: Vapor pressures of select metals [37]

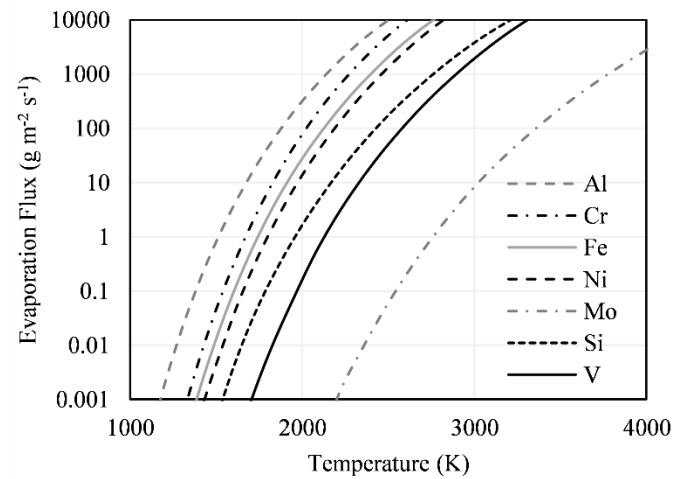


Figure 3: Evaporation flux of select metals [37]

Vanadium Producers

The industry was surveyed to determine the companies, complexes and/or facilities that are actively producing or can actively produce vanadium when it is economically favorable. Due to price fluctuations, some co-producers opt to suspend vanadium production when the price is too low. In 2018, 91% of 95,581 metric tons (mt) of vanadium produced globally were processed in China (54%), Russia (20%), South Africa (8%), Brazil (6%) and USA (3%) [23]. Table 1 presents more detailed information gathered from company websites, annual reports, technical reports, articles, and other sources.

Table 1: Vanadium producers by country (gray shading indicates producer of pure V)

Country	Complex/ Facility	Company	Source	Products	Capacity (V ₂ O ₅ mt/yr)
Austria	Althofen	Treibacher [38]	Secondary, Recycle	V ₂ O ₅ , FeV	7,000
Australia	Windimurra	Atlantic Ltd [39]	Ore	V ₂ O ₅	7,750 ^a
Brazil	Maracas-Menchen	Largo Resources Ltd [27]	Ore	V ₂ O ₅	9,300 ^b
China	Sichuan	Panzhuhua Iron and Steel [38, 40]	Ore	V ₂ O ₅ , FeV, VAl	40,000
	Hebei	Chengde Iron and Steel [40]	Ore	V ₂ O ₅ , VAl	34,000
		Chengde Tianda Vanadium [41]	Ore	VAl, V	5,200 ^c
		Other (Various) ^d	---	V ₂ O ₅ , FeV, VAl	>31,000 ^e
Czech Republic	Mníšek	EVRAZ Nikom [42]	Vanady Tula	FeV	4,940
Germany	Nürnberg	AMG GfE [43]	Secondary, Recycle	V ₂ O ₅ , FeV, VAl	
	Helba	AURA Technologie [22]	Recycle		10,000 ^f
India		Rubamin [44]	Recycle	Catalysts	20,000 ^f
Japan	Ako	Taiyo Koko [45, 46]	Recycle	V ₂ O ₅ , FeV, V	855
Netherlands	Heerlen	Moxba Metrex [47]	Recycle	V ₂ O ₅ , FeV	
Russia	Kachkanar	EVRAZ Vanady Tula [42]	Ore	V ₂ O ₅ , FeV	7,500 5,000 ^g
South Africa	Vametco, Vanchem	Bushveld Vanadium [23, 48]	Ore	V ₂ O ₅ , FeV	3,900 ^h
	Rhovon	Glencore [49, 50]	Ore	V ₂ O ₅ , FeV	9,100
South Korea	Ulsan	GS Eco Metals [51]	Recycle	V ₂ O ₅ , FeV	7,000 ^f
Taiwan	Fangliao	Hong Jing Resources Co.,Ltd. [52]	Recycle	V ₂ O ₅ , FeV	15,000 ^f
United States	Hot Springs	EVRAZ Stratcor [42]	Secondary, Recycle	V ₂ O ₅	2,750
	Cambridge	AMG Vanadium [53]	Recycle	FeV	27,300 ^{f,i}
	New Castle	AMG Titanium Alloys [54, 55]	Oxides	VAl	
	Robesonia	Reading Alloys	Oxides	VAl	
	White Mesa Mill	Energy Fuels [31]	Ore	V ₂ O ₅	870
	Freeport	Gladieux [56, 57]	Recycle	V ₂ O ₅	2,000
	Gibellini	Silver Elephant Mining (Prophecy) [58, 59]	Ore	V ₂ O ₅	5,170 ^j

^a Operations suspended in 2014 with a projected mid-2020 start, ^b 2017 production, ~11,750-12,250 tonnes expected for 2020, ^c Master alloy basis, ^d There are 40 significant producers and an estimated 150 small scale producers in China [60], ^e Difference between 2017 production of 143,000 mt and Panzhuhua and Chengde capacity[59], ^f Spent catalysis basis, ^g FeV basis, ^h FY20 projection, Vanchem's 3 kilns will increase capacity to 10,000 mt when refurbished, ⁱ Based on claims that Zanesville plant will double AMG Vanadium's capacity to 60,000 tons when completed in 2021, ^j Projected capacity when operational in 2023

For each company in Table 1, the sources of information are cited after their name. The producers are sorted and listed by country. The locations of the processing facilities or mining and extraction complexes are listed in the second column. The most recent company in ownership of the facilities or complexes are listed in the third column. The feedstock or sources accepted are listed in the fourth column. Ore is listed if the company extracts ore to produce vanadium as primary or co-product. Secondary means that company accepts vanadium rich slag from another facility and processes it into vanadium products. Recycle means that facility processes spent catalysts, oil residues, fly ash and other industrial wastes rich in vanadium. The four products listed are V₂O₅, FeV, VAl, V, although some companies also produce other minor

vanadium chemicals and alloys. The capacity is reported on V_2O_5 basis. It should be noted that the source, products, and capacity are reported based on the most recent, available information in the open literature. This is also not an exhaustive list. There are many small producers, like scrap metal recyclers (Exotech, RS-Recycling GmbH, Mississauga Metals and Alloys, etc.), who were not included, as well as vendors who source their materials from one of the facilities listed.

The current list of producers is quite different from the one published in 2003 [1]. Many producers exited the market during the last 17 years, particularly in countries with higher operating costs, like the United States, which has seen a major reduction in producers. As can be seen in Figure 4, the price of vanadium steadily declined from 2006 to 2016 aside from a spike between 2008 and 2010. This trend in vanadium prices in combination with lower cost operations caused companies to fold or divert their resources to other products. The price spiked again over the past couple years due to the loss of a major producer in Highveld Steel and Vanadium, stricter environmental regulations and higher standards for vanadium content in Chinese rebar [2–4, 23]. The price has since settled around \$13.9/kg for the past few months which is up from their low of \$5.3/kg in 2016.

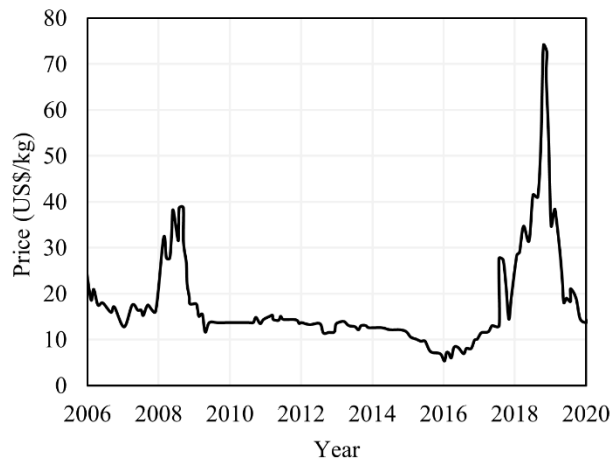


Figure 4: Price of V_2O_5 from China. Adapted from [61].

V_2O_5 and FeV are commonly produced by most of producers listed in Table 1. FeV is an additive to high-strength steel which supports many industries from automotive, construction, defense and tooling industries. V_2O_5 is used as a catalyst in sulfuric acid production and increasingly as in electrolyte in grid-level energy storage. VAl, master alloys, are used in the aerospace industry to produce titanium alloys. Only two producers (shaded in gray in Table 1) were identified as offering pure vanadium. Pure vanadium is used in strategic applications, such as the manufacturing of infrared cameras and cladding titanium to steel for airframe joints [1, 13]. Due to the specialized applications of pure vanadium, the demand is trivial in comparison to the alloy/chemical market and can be inconsistent. However, strategic uses, in which vanadium cannot be substituted, make limited producers a key vulnerability in vanadium supply. The

demand for pure vanadium is not a major driver in the vanadium market, yet is still existent. Hence, the ability to better meet that demand based on existing industry, such as VAl production, would be of strategic importance to countries that use vanadium metal in niche applications, but do not produce the metal. A limited amount of electron beam melt trials of a commercially available vanadium alloy to produce pure (>98.3 wt. %) vanadium were performed to explore the feasibility and limitations of this approach.

Feasibility of Metal Production from Master Alloy

The purity of vanadium required will vary by application and/or customer. However, two general metrics can be used to assess the performance of EBM refining. First metric is its ability to provide a higher purity than the potential alternative of reducing vanadium pentoxide with stoichiometric quantities of aluminum, which, as discussed earlier, has been reported to contain 1.7% oxygen [14]. Hence, a purity greater than 98.3 wt. % from E-beam melting would be higher than stoichiometric reduction, especially considering that other impurities are likely to be present as well. The second metric is the ability to match the current product purity. Taiyo Koko offers vanadium metal at a purity of 99.7 wt. %, establishing the second vanadium purity metric [46].

Method of Production

A 15Al-85V (wt.%) master alloy was purchased from Reading Alloys, Inc. The composition of the master alloy from the certificate of analysis provided by Reading Alloys is shown in Table 2. The net amount delivered was 251 kg (552 lb). The material was sized to be less than 8 mesh (2.38 mm) but larger than 50 mesh (0.297 mm). A 300 kW research and development (R&D) EBM furnace at Retech Systems, LLC was used to refine the master alloy. A simplified schematic of the R&D EBM furnace is provided in Figure 5 with images of the system as well. The Retech R&D EBM system feeds loose material, like the 15Al-85V granules, using a rotary drum with an internal Archimedes spiral and a vibratory chute. The loose material falls out of the rotary drum and onto the vibratory chute. The chute moves over the ingot withdrawal mold when adding material and away from the mold when the electron beam is active. This ensures reliable delivery of feed material without “shadowing” part of the top of the ingot from the electron beam, potentially resulting in partially un-melted material. It also lengthens the life of the sacrificial end of the chute by minimizing exposure to the electron beam.

Table 2: Composition of V-Al alloy from Ametek Reading Alloys

Element	Weight Percent
V	84%
Al	16%
C	0.021%
Fe	0.13%
Si	0.17%
N	0.03%
O	0.16%

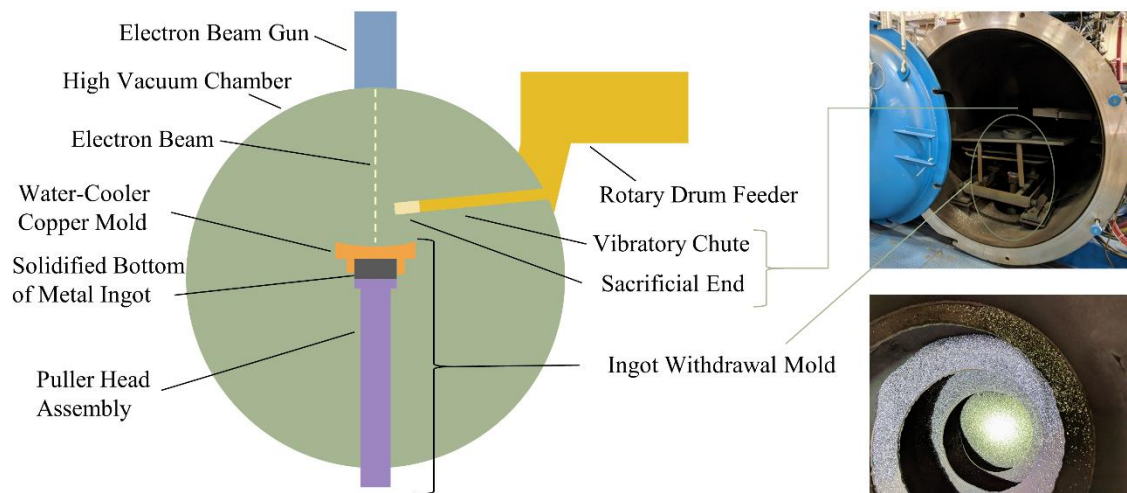


Figure 5: Simplified schematic of the Retech R&D EBM system (left), image of the inside of the vacuum chamber (top right), image of the rotary drum with an internal Archimedes spiral loaded with V-Al granules (bottom right).

The E-beam system was set up with a 15.24-cm (6-inch) diameter ingot withdrawal (IW) mold in the melt chamber. The ingot withdrawal mold consists of a water-cooled copper flange at the top, an adaptor plate, and a puller head assembly. The puller head moves downward at a withdrawal rate to make room for more material to be melted. The system was thoroughly cleaned inside to limit cross-contamination from previous melting. The melting was monitored remotely using cameras mounted on the chamber and video screens in the control room. Three runs were performed with a steady-state E-beam gun power of 80 kW and chamber pressure between 0.133-0.667 Pa (1-5 mTorr) at different dwell times (the time between alloy additions).

Melt Run #1. Approximately 45.4 kg (100 lb) of the master alloy was loaded into the rotary drum feeder. A starter button was made first from the 85V-15Al alloy feed material. Loose V-Al flakes (~1.77 kg) were placed in the IW mold on top of a flat copper adapter plate. The system was evacuated using roughing pumps to the order of 1 Pa (10 mTorr). A diffusion pump was then brought on-line to lower the pressure to about 0.1 Pa (1 mTorr). The E-beam gun was started at low power (1-2 kW) on the material. While monitoring the chamber pressure to maintain it in between 0.133-0.667 Pa (1-5 mTorr), the gun power was gradually increased to 40 kW over a period of 50 minutes. The resulting button mass was 1.0 kg which indicated that a significant portion of the material was vaporized during the melt.

The contents in the mold were completely melted forming a short button about 1.27 cm (0.5 in) tall. The puller head assembly was converted to the ingot withdrawal configuration by removing the flat copper adapter plate. The circular dovetail adapter was installed. The button was flipped on top of the circular dovetail adapter. The system was pumped down again as described above, and the dovetail casting sequence as started. Once the top of the button was completely molten,

the beam pattern was focused on the center of the button to melt through it. The molten material filled the circular dovetail assembly and solidified.

Once the dovetail was cast, feeding of the alloy material from the rotary drum started. During feeding and subsequent melt in, the chamber pressure was monitored and maintained by limiting the amount of feed material introduced to the IW mold. Upon addition of alloy material, the chamber pressure would spike. As soon as the chamber pressure dropped back down to its baseline of about 0.133-0.400 Pa (1-3 mTorr), another small quantity (approx. 600g) of the loose material was fed. The average feed & melt-in cycle time was 1 minute for the first ingot. Due to the slow feeding needed for refining, multiple 8 hour melting days were used to make the full 101.6 cm (40 in) length ingot. Each day, the same process conditions as described above were used. After the last addition, the system was shut off and allowed to cool overnight.

After the chamber doors were opened the following day, a noticeable amount of feed material was discovered on the chamber floor and the mold shield. After removal of the ingot from the chamber, samples were taken from the top, middle and the bottom using a 0.95 cm (3/8 in) drill bit. The amounts of drill bit turnings were approximately 50 g from each location. These samples were sent to Northern Analytical Lab in Londonderry, New Hampshire for chemical analysis. Northern Analytical Lab performed Glow Discharge Mass Spectroscopy (GDMS) for total metals and combustion analysis for carbon, hydrogen, nitrogen, and oxygen on all samples for every run. The dovetail end of the ingot was cut off using a band saw to yield a 40 inches long ingot. A photo the ingot after cutting is displayed in Figure 6. The ingot weight after sampling and final cutting to 101.6 cm (40 in) was 103 kg (226 lb). The feed material remaining in the shipping drum weighed 80 kg (176 lb). 171 kg (376 lb) was consumed during melting of the first ingot.



Figure 6. Ingot from melt run #1 after removing the dovetail

Melt Run #2. The same processing methods and conditions were used, except the feed and melt-in cycle time (i.e., dwell time) was doubled to 2 minutes. The rotary feeder was reloaded and the dovetail from run #1 was used in the IW mold. During preheat and melting of the stub, the circular copper dovetail adapter was completely melted. The thin (only 3.175 mm) amount of material on the starter dovetail was not enough to withstand the power used (≤ 80 kW) while melting and adjusting the beam focus. A new circular copper dovetail was made. Similar to the first ingot, 1.59 kg (3.5 lb) of loose material was placed in the mold on top of the flat copper adapter plate. After the new starter stub was reformed, a 15.24-cm (6-inch) long ingot was created. The ingot weight was 15.9 kg (35 lb). A thin slice was cut from the top of the ingot with a band saw. A 2.54-cm (1-inch) wide strip was cut from this disk from the center. This strip was sent to Northern Analytical Labs for chemical analysis.

Melt Run #3. The remaining 14.6 cm (5.75 in) of the ingot from melt run #2 was placed back in the IW mold and used to start the next melt which was performed at the same conditions as the previous runs, except a dwell time of 4 minutes was used. The ingot was preheated for about 42 minutes with beam power gradually increased from 5 kW to 55 kW. Feed material was not initially introduced to ensure that the ingot would not stick in the mold preventing proper withdrawal motion. After the initial testing, the ingot was preheated for 28 minutes before feeding. Due to the slower feed rate, it took 3 days to feed the remaining material. The ingot was removed the chamber and cut with a band saw at 14.6 cm (5.75 in) from the dovetail end position. A thin slice about 3.175 mm (1/8 in) thick was cut from the bottom and the top of the

third ingot. A 2.54-cm (1-inch) wide strip was cut from the center of both disks. These strips were sent to Northern Analytical Labs for chemical analysis.

Results and Discussion

The results of the chemical analysis are given in Table 3 for any element detected above 10 ppm in any of the melts. A sample from the feed material was analyzed by Northern Analytical Labs by ICP-MS and ICP-OES to determine the concentration of metallic impurities. The ICP-MS analysis of metallic impurities differed slightly with the values listed in Table 2. The purity of V was lower and the concentration of Si, Fe and Al was higher than the certificate of analysis values. As described earlier, the dwell time increased from the 1st melt to the 3rd melt. The purity of vanadium increased with dwell time up to 99.3%, which is between the two general purity metrics of 98.3 and 99.7 wt. %.

Table 3: Composition (wt. %) of electron beam melted vanadium ingots

Element	V-Al Alloy Feed	1st melt	1st melt	1st melt	2nd melt	3rd melt
		Top	Middle	Bottom	Top	Top
V	82.7%	97.43%	97.37%	98.35%	99.15%	99.34%
Al	16.7%	2.00%	2.00%	1.10%	0.290%	0.0675%
Si	0.20%	0.30%	0.32%	0.31%	0.40%	0.46%
O	0.16%	0.051%	0.041%	0.039%	0.012%	0.010%
Fe	0.15%	0.12%	0.12%	0.074%	0.059%	0.054%
N	0.03%	0.051%	0.055%	0.060%	0.023%	0.015%
Ti	0.028%	0.0095%	0.0095%	0.013%	0.012%	0.011%
C	0.021%	0.016%	0.020%	0.018%	0.018%	0.016%
Ni	0.0060%	0.0070%	0.0075%	0.0045%	0.0040%	0.0055%
W	0.0035%	0.0021%	0.0022%	0.0025%	0.0023%	0.0026%
P	<0.0025%	0.011%	0.011%	0.0090%	0.014%	0.016%
S	---	0.0036%	0.0038%	0.0019%	0.0035%	0.0035%
Mo	0.0020%	0.0090%	0.010%	0.0095%	0.010%	0.013%
Co	0.0016%	0.013%	0.014%	0.0080%	0.0088%	0.011%
B	<0.0010%	0.0017%	0.0018%	0.0012%	0.0011%	0.0015%
H	---	0.00050%	0.00050%	0.00050%	0.0028%	0.0020%

The trend of vanadium and aluminum content with dwell time is given in Figure 7. To quantify this trend, a half-life model was used in equation (2), similar to nuclear decay, where the half-life is the time required for half of the material to be removed.

$$C(t) = C(0)2^{-t/t_{0.5}} \quad (2)$$

$t_{0.5}$ is the half-life, C is the concentration in wt. %, t is dwell time. Using this model, the half-life for Al in our tests is 18.3 seconds. The model for vanadium is generated by simply subtracting

the total impurity concentration from 100% (i.e., $1 - C(t)$). The half-life calculated from fitting the vanadium content is 20.7 seconds and can be considered the total impurity half-life. The trends for the content of minor impurities with increasing dwell time are decreasing for O, Fe, Ni, C; increasing for Si, P, Mo, H; and relatively constant for Co, Ti, S, W, B. The trends of the elements increasing with dwell time, with exception of H, are given in Figure 8. Like V and Al, half-lives were determined to be 76.3, 43.2 and 42.3 seconds for Si, P, and Mo, respectively. The trend of H was not evaluated because its initial value is unknown.

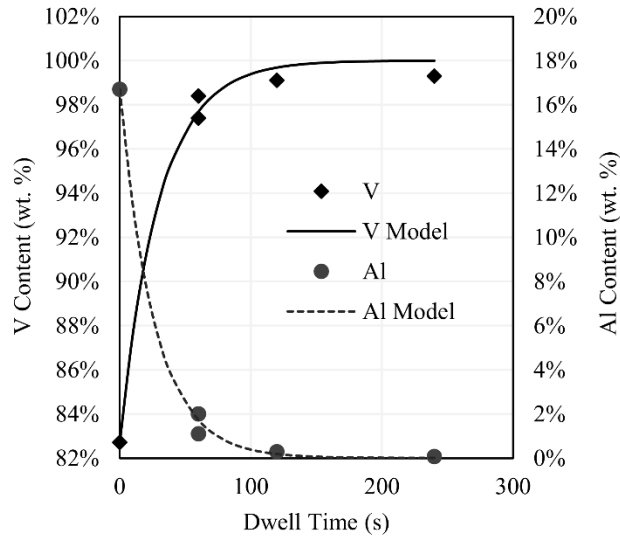


Figure 7: The trend of V and Al with dwell time

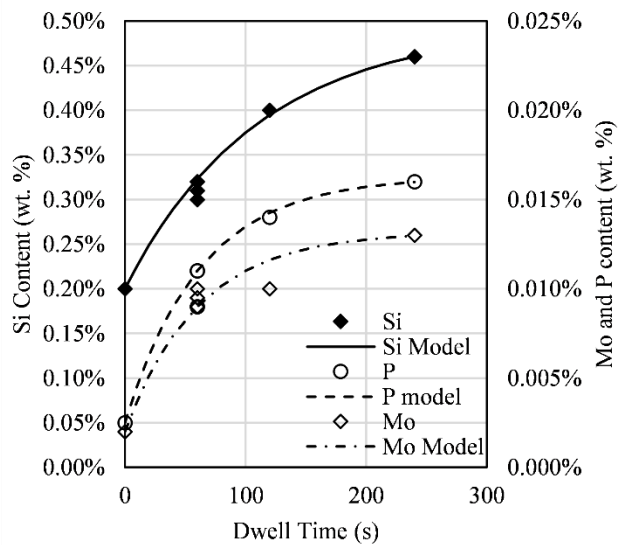


Figure 8: The trend of Si, P, and Mo with dwell time

Most of the impurities in the V-Al alloy feed are ≤ 0.03 wt. % and do not significantly impact the final purity of vanadium. Si, Fe and O are the only impurities >0.03 wt. % in the feed. Despite Fe and O having relatively high impurity levels, both decrease with dwell time. O was removed to below 0.03 wt. %. Based on the trend of Fe, it could be reduced to 0.03 wt. % with a dwell time of 6 minutes. The increasing trend for Si and H is unexpected. Fortunately, the initial concentration of H is low enough that it does not build to a significant level. On the other hand, Si reaches nearly 0.5% and begins to limit the purity of V achievable.

Based on Table 2, the amount of Si in the 251 kg fed was 0.427 kg. If none of the Si vaporized, then the expected concentration in the V ingots would have been 0.277 wt. %. This estimate does not agree with the approximate 4000 ppm (or 0.4 wt.%) measured in the ingots by GDMS in Table 3. Consequently, if the Si content in the feed of 0.20 wt. % as measured by ICP-OES from Table 3 is used, then the expected concentration becomes 0.332 wt% which matches well with melt #1. To confirm the assumption of no or minimal Si evaporation, the condensate on the E-beam chamber was analyzed with ICP-OES and Si content was found to be only 0.025 wt. % while Al and V were 48.6 and 48.1 wt. %, respectively. Hence, Si essentially remained in the ingot.

In Figure 3, the evaporation flux of Si was predicted to be higher than V, yet more V was found in the condensate. The calculated values in Figure 3 assumed no interaction in the liquid phase and are given per unit area. Based on V-Si phase diagram, there is interaction between V and Si [62]. In fact, a V_5Si_3 compound can form with a melting point of 2100°C which is above that of V and Si. Hence, there may be significant non-ideal behavior of Si in molten V. Also, to consider, is that Si is present at considerably lower concentration than V which likely resulted in significantly less Si available at the melt surface for evaporation. Hence, although, the evaporation flux of Si is higher than V, the disparity in availability at the surface may have resulted in a Si evaporation rate significantly less than that of V. Thus, if a low silicon content is required, the feed material must be less than half of the specified limit based on the melt results.

The data collected for the masses in the feed and product are given in Table 4. Unfortunately, since the 3rd melt was essentially a continuation of 2nd the melt, the feeder was not removed and weighed between those melts. Hence only a combined loss and yield can be calculated for the 2nd and 3rd melt. The 1st melt has more loss and lower yield due to the spillage that occurred. Due to their small size, the spilled VAl flakes and other processing debris could not easily be separated to determine an accurate mass of the spillage. The spilling was resolved for the 2nd and 3rd melt. The spilled VAl flakes artificially reduce the vanadium yield in the 1st melt. Considering the spillage in the 1st melt, the yields and mass losses are still similar between all three melts while the dwell time increased from 1 to 4 minutes. Consequently, the effect of the spillage in the 1st melt was likely minimal and the dwell time does not appear to have a significant effect on yield.

Table 4: Mass, loss, and yield data from each melt

	1 st Melt	2 nd Melt	3 rd Melt
Feed Mass (kg)	171	80.0	
Ingot Mass (kg)	103	15.9	35.0
Mass Loss (%)	39.8%	36.4%	
V in Feed (kg)	144	67.2	
V in Ingot (kg)	106	50.5	
V Yield (%)	73.6%	75.1%	

Future E-beam melting and refining of the 85V-15Al master alloy should consider longer daily operation of the system. A 24 hr/day operation would be ideal to minimize the total processing time. When only using a maximum of 10 hr/day operation, too much time is spent in preheating the system (about 1 hour) at the start of the day and cool down of the diffusion pumps (about 2 hours) at the end of the day.

Assuming a processing rate of 0.3 mm of ingot per minute (~4 min. dwell time) to achieve V purity above 99%, the equivalent melt rate would be 1.8 kg/hr (4 lb/hr) at a chamber pressure of 0.266 Pa (2 mTorr). Future efforts should consider the use of a larger surface area molten pool to increase throughput. A refining hearth in combination with the ingot withdrawal mold could be beneficial provided the system's vacuum pump capacity has been correctly sized.

Conclusion

The vanadium industry has changed significantly within the last 17 years with producers in the Americas and Europe exiting the market. Vanadium oxides, chemicals and alloys are readily available in multiple countries and can be produced at high purity. Most of the oxides produced are reduced and processed with iron to make ferrovandium which is used to make high-strength steel for construction, defense, and tooling. A small amount of the oxide is also reduced with aluminum to form master alloys (V-Al alloys). The master alloys are mostly used to make Ti-Al-V alloys for the aerospace industry. Another small portion of the vanadium oxide remains in oxide form to be used as a catalyst or as feedstock for VRFB. The amount of production of pure vanadium metal is trivial in comparison to the quantities produced of alloys and oxide. This is due to specialized use of the metal. However, this metal is still required in strategic applications and only two producers were identified. Vanadium metal can be produced from commercially available V-Al alloy via electron beam melt refining. Three trials were run with increasing vanadium purity from 97.4 to 99.3 wt. % as dwell time increased from 1 to 4 minutes. To achieve >99% V, it is recommended to process at 0.3 mm of ingot per minute at a chamber pressure of 0.266 Pa. Faster processing times could be achieved by using an EBM furnace equipped with a refining hearth. The 2nd and 3rd melts exceeded the purity expected from stoichiometric reduction of V₂O₅ (98.3%), but did not reach the purity (99.7%) offered by an existing supplier. The limiting factor in the purity of V was the presence of Si which increased with dwell time.

EBM furnaces constitute a significant capital equipment investment on the order of millions of dollars and require skilled technicians to operate. Fortunately, they are a commonly used technology for purifying reactive and refractory metals (e.g., Ti, Ta, Nb). Consequently, many countries already employ this technology in the production of other metals and could leverage their existing capabilities, if needed. Hence, EBM refining of available alloys provides a simple, single-step process using existing infrastructure to mitigate potential vanadium supply risks.

This work adds data to the public domain on the EBM refining of commercially available vanadium alloys. Countries, companies, engineers, and researchers can utilize these EBM refining results to verify, examine, or develop the technical aspects of leveraging industrially available sources of V-Al alloys to obtain pure V in efforts to diversify their supply of pure V.

Acknowledgement

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. The authors also wish to acknowledge the assistance of Matthew Duncan and Robin Lampson in operating the electron beam furnace.

Conflict of Interest: The authors declare that they have no conflict of interest.

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