

Vanadium and Vanadium Compounds

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1. History [1]

In 1801, MANUEL DEL RIO discovered vanadium in Mexican lead vanadate ore. In 1831, SEFTSTRÖM detected the element in converter slags from certain iron ores, and named it after the Norse goddess of beauty, Vanadis.

Vanadium metal was first produced in powder form by ROSCOE in 1867–1869 by reduction of vanadium dichloride with hydrogen. MARDEN and RICH obtained ductile vanadium by reducing vanadium pentoxide, V_2O_5 , with calcium metal.

The first major application of vanadium was in 1903 in England, where a vanadium-alloyed steel was produced on an 18 t scale [2]. In 1905 HENRY FORD recognized the advantages of vanadium steel and promoted its use in automobile construction. Today vanadium is of major importance as an alloying component in steel and

titanium alloys and as a catalyst for chemical reactions.

2. Properties

Vanadium [7440-62-2], V, atomic number 23, has two stable isotopes: ^{51}V (99.75 %) and ^{50}V (0.25 %). Unstable isotopes of relative atomic mass 48, 49, and 52 have half-lives ranging from 4 min to 600 d. The electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. Vanadium is steel gray with a bluish tinge. It is ductile, and can be forged and rolled at ambient temperature.

Vanadium, together with niobium and tantalum, belongs to group 5 of the periodic table. It has a high melting point and good corrosion resistance at low temperature.

Physical Properties. The most important physical properties of vanadium are listed in the following [1], [3–6]:

Relative atomic mass	50.9415
Crystal structure	body-centered cubic
Lattice constant a	0.30238 nm
Density	6.11 g/m ³
mp	1929 °C \pm 6
Heat of fusion	21 500 J mol ⁻¹ \pm 3000
Specific heat, J mol ⁻¹ K ⁻¹	
at 298 K	24.35 \pm 0.10 J mol ⁻¹ K ⁻¹
for 298–900 K	$C_p = 24.134 + 6.196 \times 10^{-3} T$ $- 7.305 \times 10^{-7} T^2 -$ $1.3892 \times 10^{-5} T^{-2}$
for 900–2200 K	$C_p = 25.9 - 1.25 \times 10^{-4} T +$ $4.08 \times 10^{-6} T^2$
for liquid V	47.43 J mol ⁻¹ K ⁻¹
Vapor pressure	
at 2190 K	3.73 Pa
at 2200 K	4.31 Pa
at 2300 K	12.53 Pa
at 2400 K	30.13 Pa
at 2500 K	87.86 Pa
at 2600 K	207.6 Pa
for liquid V, mbar	$\log p = -24.265 \times 10^3 T^{-1}$ $+9.65$
Heat of vaporization	465.9 kJ mol ⁻¹
Linear coefficient of expansion	
at 20–200 °C	7.88×10^{-6}
at 20–500 °C	9.6×10^{-6}
at 20–900 °C	10.4×10^{-6}
at 20–1100 °C	10.9×10^{-6}
Specific electrical resistivity at 20 °C	$24.8 \times 10^{-6} \Omega \text{ cm}$
Temperature coefficient for 0–100 °C	$0.0034 \mu\Omega \text{ cm K}^{-1}$
Thermal conductivity	
at 100 °C	$0.31 \text{ J cm}^{-1} \text{ K}^{-1} \text{ s}^{-1}$
at 500 °C	$0.37 \text{ J cm}^{-1} \text{ K}^{-1} \text{ s}^{-1}$
Superconductivity, transition temperature	5.13 K
Capture cross section for thermal neutrons	4.8 barn

Mechanical Properties. The mechanical properties of vanadium are strongly dependent on purity and hence on the production method used. In particular, the elements O, H, N, and C increase the hardness and tensile strength and decrease the ductility (elongation) [7]. The most important mechanical properties are listed in Table 1 [3], [4], [7].

Table 1. Mechanical properties of vanadium metal

	Commercial purity	High purity
Tensile strength σ_B , N/mm	245–450	180
Extension, %	10–15	40
Vickers hardness HV 10, N/mm	80–150	60–70
Modulus of elasticity, N/mm	137 000–147 000	
Poisson's ratio	0.35	

Chemical Properties. Vanadium is stable in air below 250 °C. On prolonged storage the surface becomes bluish-gray to brownish-black, and significant oxidation takes place in air above 300 °C. Vanadium absorbs hydrogen in interstitial lattice sites at elevated temperatures (up to 500 °C). The metal becomes brittle and can easily be powdered. This hydrogen is liberated on heating to 600–700 °C in vacuum. At low temperature, a hydride phase exists in the V–H system [7]. Vanadium reacts with nitrogen at > 800 °C to form vanadium nitrides. It has a high affinity for carbon, forming carbides at 800–1000 °C. Data on the solubility of O, N, H, and C in vanadium and the reactions that occur with these elements can be found in [7], [8].

In its compounds, vanadium exhibits the oxidation state II, III, IV, or V. It is relatively stable towards dilute sulfuric, hydrochloric, and phosphoric acids, but is dissolved by nitric and hydrofluoric acids. Its corrosion resistance towards tap water is good, and towards seawater moderate to good, but pitting does not occur. Vanadium is resistant to 10 % sodium hydroxide solution, but is attacked by a hot solution of potassium hydroxide [1], [3], [4], [9], [10]. Vanadium and some vanadium alloys have good corrosion resistance towards molten low-melting metals and alloys, especially alkali metals, which are used in nuclear reactors as coolants and heat-exchange media [11].

3. Occurrence

Vanadium is present in the earth's crust at a mean concentration of 150 g/t, and is therefore one of the more common metals. It is more abundant than copper and nickel, and of similar abundance to zinc. Vanadium forms several minerals, of which the most important are listed in Table 2 [12], [13].

In the early 1900s, vanadium was obtained almost exclusively from Peruvian patronite. As these deposits became exhausted, descloizite ores were mined in southern Africa, Namibia, and Zambia.

After World War II, the continental sedimentary uranium- and vanadium-containing carnotite deposits of the Colorado Plateau and the marine sedimentary vanadium-bearing phosphate deposits of Idaho became important. There

Table 2. Principal vanadium minerals [12], [13]

Mineral and chemical formula	Vanadium content, %	V ₂ O ₅ content, %	Occurrence
Roscoelite [KV ₂ (OH) ₂ /AlSi ₃ O ₁₀]	11.2–14.0	20–25	in uranium–vanadium ores; e.g., Colorado Plateau, United States
Montroseite (V, Fe)OOH	45.4	81.0	
Carnotite K ₂ [(UO ₂) ₂ /V ₂ O ₈] · 3 H ₂ O	10.3	18.3	
Tyuyamunite Ca[(UO ₂) ₂ /V ₂ O ₈] · 5–8 H ₂ O	11.1	19.8	
Francevillite (Ba, Pb)[(UO ₂) ₂ /V ₂ O ₈] · 5 H ₂ O	9.9	17.7	
Corvusite V ₂ ⁴⁺ · V ₁₂ ⁵⁺ O ₃₄ · n H ₂ O	40.8	72.8	
Vanadinite Pb ₂ [Cl/(VO ₄) ₃]	10.2	18.2	in Pb, Zn, Cu vanadate ores; e.g., Otavi Mountains, Namibia
Descloizite Pb(Zn, Cu)[OH/VO ₄]	12.7	22.7	
Mottramite Pb(Cu, Zn)[OH/VO ₄]	10.5	18.8	
Patronite VS ₄ or V ₂ O ₅	16.8	ca. 30	in asphaltes; e.g., Mina Ragra, Peru
Magnetite* Fe ₂ ²⁺ · Fe ³⁺ O ^{4–}	< 0.5–1.5	< 1.2–2.7	in titanomagnetite ores; e.g., Bushveld, Republic of South Africa
	max. 2.8	max. 5.0	

* Several varieties exist in which there is partial replacement of Fe³⁺ by V, Ti, Al, and Cr, and of Fe²⁺ by Ti, Mg, Mn, and other elements. The vanadium- and titanium-containing magnetites are generally referred to as titanomagnetites.

are also uranium–vanadium reserves in Yeelirrie, Western Australia, and in the Ferghana Basin the Kirghiz, Tadzhik, and Uzbek Republics [13].

Vanadium production greatly increased from the mid-1950s with the mining and processing of titanomagnetites. This type of raw material can be used directly for vanadium extraction, or it can be employed to obtain vanadium-containing pig iron from which an oxidation slag highly enriched in vanadium is produced. This development began in Finland, followed by South Africa and smaller producers in Norway and Chile. Titanomagnetites have also been mined in the former Soviet Union and China in large quantities since the early 1960s and 1970s, respectively. The vanadium-bearing titanomagnetite deposits are of magmatogenic origin, and occur in many parts of the world. The most important reserves mined today include the Bushveld deposit in South Africa, Katschkanor in the Urals of Russia, Lanshan and Chienshan in the Sichwan province of China, and a deposit in New Zealand. The titanomagnetites of the Urals and in the Sichwan province are palaeozoic complexes.

The mines at Otanmäki and Mustavaara in Finland and Rødsand in Norway were shut down during the 1980s.

Production of lead–zinc vanadates in Namibia had been discontinued by the end of the 1970s.

Since the 1980s, a new type of secondary raw materials has gained importance, i.e., residues of mineral oil processing. Most crude oils contain vanadium in amounts ranging from ca. 10 ppm (Middle East) to 1400 ppm (Central America). In petrochemical refining, vanadium is retained in boiler residues and fly ashes from incineration, with vanadium contents between a few percent and 40 %. The total amounts greatly exceed current world consumption.

Noteworthy is an aqueous emulsion of a highly viscous crude from the Orinoco basin in Venezuela (Orimulsion) whose combustion yields fly ashes containing 10 % vanadium.

With environmental legislation becoming stricter, emission and deposition of these residues will be drastically reduced so that they will have increasingly to be processed.

Table 3. Vanadium production as a byproduct

Raw material	Coupled product	Vanadium byproduct
Titanomagnetites	iron/steel	vanadium slag
Mineral oils	energy/petrochemicals	fly ashes boiler residues
Uranium–vanadium ores	uranium	petrochemical residue
Bauxite	alumina	vanadium salt
Phosphates	phosphorus	vanadium-containing Fe–P salamander
Lead vanadates	lead, zinc	vanadium slag

Other, less important vanadium sources are: vanadium-containing waste salts from bauxite

production, and spent catalysts from the chemical and petrochemical industries. The extraction of vanadium from currently available raw material sources (except direct processing of titanomagnetite) is always coupled with the production of other metals or energy. The most important sources are shown in Table 3.

Resources and Production. Known and estimated mineral reserves are listed in Table 4.

In this table the vanadium containing carbonitic shells (very low concentration) and the petroleum ashes/residues are not included, although these oils contain tremendous amounts of vanadium.

Assessment of world reserves by studying the geology of deposits suggests that it will be possible to discover further workable deposits in the region of the widely distributed titanomagnetites in the old shields. The Indian shield in the Singbhum (Bihar) and Magurbhanj (Orissa) regions, the Australian shield in Western Australia, the Canadian shield in Quebec and Ontario, and the Finno-Scandinavian shield all show great promise. However, little is so far known about the Brazilian shield. The enormous vanadium reserves in the titanomagnetites cannot yet be even approximately quantified.

The world production of vanadium by country is listed in Table 5 [14].

Comparison of Tables 4 and 5 shows that the largest producers, the Republic of South Africa and Russia, have also the largest mineral reserves. The next two producing countries China and the United States have comparatively small reserves of such origin.

Details of the Most Important Deposits.

The Bushveld deposit in South Africa is an oval, bowl-shaped complex in a magmatic layer extending over an area of 65 000 km². The ores were deposited in the following order: chromite, platinum ores, vanadium-containing titanomagnetites, and tin ores. In all, 21 magnetite layers have been found in the main and upper zones of this deposit. The titanomagnetites have the following chemical composition (%):

Fe	55.8–57.5	Cr ₂ O ₃	0.13–0.45
V ₂ O ₅	1.4–1.6	Al ₂ O ₃	2.5–3.5
TiO ₂	12.2–13.9	SiO ₂	0.9–1.5

The V₂O₅ content can be as high as 2.4 % in exceptional cases.

Production by Highveld Steel & Vanadium is based on ore containing 1.6 % V₂O₅ from the Mapochs mine, situated 90 km NNE of Middleburg. The reserves contain 200×10⁶ t ore. Mining is by the open pit method, and the maximum ore production capacity is 8000 t/d [13].

Other South African titanomagnetite deposits include the Kennedy's Vale mine, with a production capacity of 6000 t/d (though not currently producing) and two mines near Brits, each with a production capacity of 5000–6000 t/d.

There are a number of lead vanadate deposits in the Otavi Mountains in Namibia. Mount Aukas, near Grootfontein, has deposits of 2×10⁶ t ore containing 15 % Zn, 4 % Pb, and 0.5 % V₂O₅. Deep mining has been discontinued since 1978. The mined ore, which was processed by flotation, yielded the following products: lead sulfide concentrate, zinc sulfide concentrate, willemite concentrate, cerussite concentrate, and a vanadium concentrate containing 17 % V₂O₅, 43 % Pb, and 17 % Zn.

The titanomagnetite deposits at Otanmäki and Mustavaara in Finland had reserves of 15×10⁶ t ore containing 35–40 % Fe, 13 % TiO₂, and 0.45 % V₂O₅, and 40×10⁶ t ore containing 17 % Fe, 3.1 % TiO₂, and 0.36 % V₂O₅ [14]. The production capacity of the Otanmäki deep mine was ca. 1×10⁶ t/a ore. Magnetite containing 69 % Fe, 2.5 % TiO₂, and 1.07 % V₂O₅ together with ilmenite and pyrite were obtained by magnetic separation and flotation. Both mines were closed in the 1980s.

The Colorado Plateau in the United States contains the main mining area of the Uravan mineral belt, > 1100 km long, in SW Colorado and SE Utah. This belt contains irregular lenticular ore bodies, normally < 3000 t, with 0.2–0.3 % U₃O₈ and 0.85–1.4 % V₂O₅. The oxidation region contains the minerals carnotite, tyuyamunite, montroseite, and pascoite, and the unoxidized region contains the minerals coffinite, pitchblende, and curvusite. These ores are extracted in small deep mine workings which produce ca. 0.4×10⁶ t/a ore.

Table 4. Estimate of the world reserves and reserve base of vanadium in thousand tonnes of vanadium content (percentage given in parentheses)

Geographic area	Reserves		Estimated reserves
	1985	1990	1985
North America	185 (4.0)	135 (3.2)	2500 (13.7)
South America	25 (0.5)		130 (0.7)
Former Soviet Union	2900 (60.4)	2631 (61.7)	4500 (24.6)
South Africa	950 (19.7)	862 (20.2)	8600 (47.0)
China	670 (14.0)	500 (14.2)	1800 (9.8)
Pacific	35 (3.1)	30 (0.7)	570 (3.1)
Total	4800 (100)	4267 (100)	18 300 (100)

Table 5. World production of vanadium-containing commodities by country, given in tonnes of vanadium content [14]

Countries	1985	1986	1987	1988	1989	1990	1991	1992	1993
China ^a	5 500	5 500	5 500	5 500	4 500	4 500	4 500	4 500	5 000
Finland	2 590								
South Africa ^b	17 000	18 600	17 300	19 900	16 500	17 000	15 500	14 300	16 000
Former Soviet Union	11 500	11 500	11 600	11 600	9 600	9 600	8 000	6 000	7 900
United States (total)	4 000	3 600	3 800	3 500			5 600	5 300	5 500
from catalysts and ashes	2 970	2 560	2 760	2 480					
Japan ^c	925	1 020	1 020	1 020			600	800	
New Zealand							2 200	1 700	
Total	45 700	44 000	42 100	45 300	31 600	31 600	35 800	33 200	34 500

^a Estimated.^b South Africa; roughly 40 % is pentoxide and vanadate products and 60 % is vanadiferrous slag products.^c Spent catalyst and petroleum ashes.

4. Processing of the Raw Materials to Vanadium Compounds

The raw materials used today include the titanomagnetite ores and their concentrates, which are sometimes processed directly, vanadium slags derived from the ores, oil combustion residues, residues from the hydrodemetallization (HDM) process, and spent catalysts (secondary raw materials). A summary of the processing routes is given in Figure 1.

4.1. Iron Ores and Titanomagnetites as Raw Materials

Production of Vanadium Slags. The titanomagnetite ore in lump form, containing ca. 1.51–1.7 % V_2O_5 (Mapoch mine in South Africa), is first prerduced by coal at ca. 1000 °C in directly heated rotary kilns. A further reduction is then performed in an electric arc furnace to obtain a pig iron which contains ca. 1.4 % V_2O_5 . The slag that is also formed contains ca. 30 % TiO_2 , and this is deposited on slag heaps.

In a heat resistant shaking ladle the molten pig iron is oxidized with oxygen lances, causing the vanadium to be transferred to the slag. The vanadium slag contains vanadium in the form of a water-insoluble trivalent iron spinel, $FeO \cdot V_2O_3$, at a concentration corresponding to ca. 25 % V_2O_5 . This slag is the world's principal raw material for vanadium production [16].

The largest slag and vanadium producer in the western world is South Africa (see Table 5), most of whose production is by the Highveld Steel and Vanadium Corp. [13]. Second largest producer is the Nizhny Tagil metallurgical plant in Russia; the slag contains ca. 12–18 % V_2O_5 . Another producer of vanadium slag is the Pan-nang steelworks in Panzihua, China.

Vanadium slags were produced experimentally by W. L. GOODWIN and W. P. FIRTH in 1919, but the basic industrial process was developed by R. VON SETZ, and was first used by the Spigerverk plant in Oslo in the early 1930s. The process was then mainly used in conjunction with the Thomas process. The pig iron from the blast furnace was not directly converted to Thomas steel with addition of lime in the usual way. Instead, the vanadium was oxi-

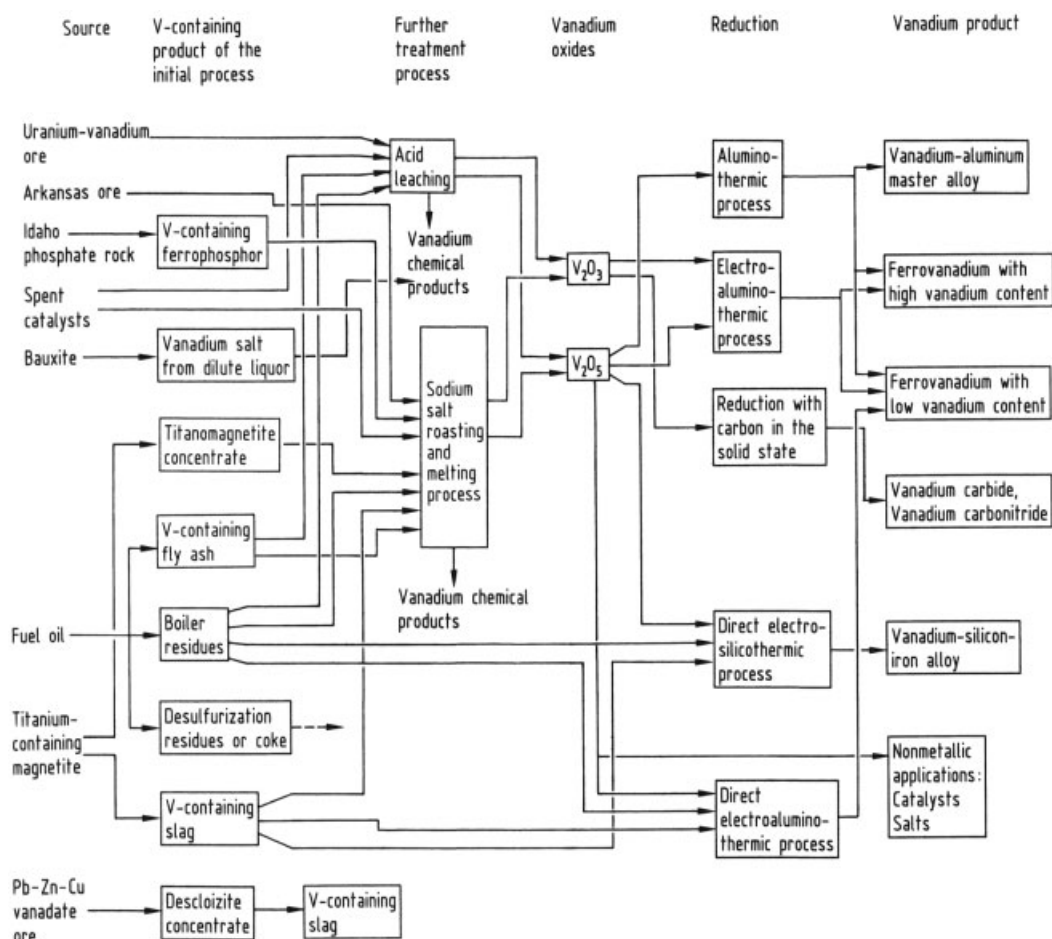


Figure 1. Treatment of vanadium raw materials [15]

dized completely or partially before lime addition. As vanadium has a high affinity for oxygen, it was oxidized before the phosphorus and transferred to the slag. Slags containing several percent of vanadium were obtained, depending on the vanadium content of the pig iron, whereas normal Thomas slags contain an average of only 0.5 % V.

Oxidation of vanadium-containing pig iron to give vanadium-containing slag was carried out by the Röchling Iron and Steel Works in Völklingen from 1937 using a converter with a very acid lining or a continuously operating oxidizing drum. For details of these abandoned processes see [17].

Processing of Vanadium Slags. The main process used today to produce vanadium oxide from vanadium slags is alkaline roasting. The same process, with minor differences, is also used for processing titanomagnetite ores and vanadium-containing residues.

A vanadium slag has the following approximate composition: 14 % V (=25 % V_2O_5), 1.5 % Ca, 2.5 % Mg, 2.0 % Al, 0.01 % P, 9 % metallic Fe, 32 % total Fe, 7 % Si, 3.5 % Mn, and 3.5 % Ti. The presence of the elements Ca, Mg, and Al, which form water-insoluble vanadates during alkaline roasting, leads to a reduction in yield. Silicon can cause filtration difficulties during leaching of the calcine. Phosphorus, unless removed in a separate treatment, reports practically quan-

titatively to the vanadium oxide, and lowers the vanadium yield in the precipitation process.

The process is shown schematically in Figure 2. The vanadium slag is first ground to $< 100\ \mu\text{m}$ (1–11 in Fig. 2), and the iron granules contained therein are removed. Alkali metal salts are then added, and the material is roasted with oxidation at $700\text{--}850\ ^\circ\text{C}$ in multiple-hearth furnaces or rotary kilns (12–20) to form water-soluble sodium vanadate. During roasting, care must be taken to prevent agglomeration of the material by sintering and to ensure rapid cooling after the material leaves the furnace. The roasted product is leached with water (21 in Fig. 2), and ammonium polyvanadate or sparingly soluble ammonium metavanadate is precipitated in crystalline form from the alkaline sodium vanadate solution by adding sulfuric or hydrochloric acid and ammonium salts at elevated temperature (22–28). These compounds are converted to high-purity, alkali-free vanadium pentoxide by roasting. The usual commercial “flake” form of vanadium pentoxide is obtained by solidifying the melt on cooled rotating tables (29–31 in Fig. 2).

The aluminothermic production of ferrovanadium is shown in Figure 2 (32–34), as well as wastewater purification (35–44), including the reduction of Cr(VI) to Cr(III) (35) and the crystallization of sodium sulfate (37).

In Russia, a combination of alkaline roasting and sulfuric acid leaching is used. A disadvantage of this process is the manganese content of up to 2 % in the V_2O_5 , caused by acid leaching.

Direct Production of Vanadium Oxide from Titanomagnetite Ores and Clays. If the ores contain $> 1\%$ vanadium, they can be directly converted to vanadium pentoxide. The gangue material is first removed from the ore by flotation, and the ore is then mixed with sodium carbonate, pelletized, and roasted in shaft furnaces or rotary kilns at $1000\ ^\circ\text{C}$. The sodium metavanadate formed is leached out with water, and vanadium pentoxide is obtained from this by the same method as that used in the roasting process for vanadium slags. The leach residue is used to produce pig iron if its ilmenite content is sufficiently low [15].

4.2. Processing of Other Raw Materials

Hydrometallurgical methods or a combination of pyrometallurgical and hydrometallurgical processes are used to produce vanadium oxides and salts from other raw materials. In the combined processes, thermal treatment is followed by alkaline or, more rarely, acid processing.

Acid Processes. Vanadium-containing oil residues and spent catalysts are digested with sulfuric acid, often under reducing conditions with addition of SO_2 . After removal of the impurities, the solution is oxidized, and polyvanadate and calcium or iron vanadate are precipitated by partial neutralization of the acid [13].

Acid digestion was formerly an important method of treating carnotite, a uranium–vanadium ore. After the uranium had been removed from the solution in sulfuric acid by solvent extraction, the vanadium was partially reduced with iron powder and solvent extracted. After re-extraction, the vanadium was in the form of an acid solution of vanadyl sulfate. This was oxidized with sodium chlorate at elevated temperature, and precipitated as red cake, a mixture of sodium and ammonium polyvanadate, by adding ammonia or ammonium salts. This precipitate was roasted to convert it into alkali-containing V_2O_5 [13], [18].

Historically, Pb–Zn–V concentrates from Namibia were subjected to acid treatment process. However, the mining of these ores became uneconomic and was discontinued in 1978.

The ore concentrate produced by flotation was ground and leached with dilute sulfuric acid (10–15 %). This led to the formation of insoluble lead sulfate. The solubility of the vanadium was considerably increased by simultaneously passing SO_2 through the liquor. Phosphorus was removed by adding sodium zirconate to precipitate sparingly soluble zirconium phosphate. The filtrate, which contained mainly ZnSO_4 and VOSO_4 , was treated with H_2S to precipitate As and Cu. The pH of the clear solution was increased to 1–2 by addition of sodium carbonate, and tetravalent vanadium was oxidized to the pentavalent state by heating with sodium chlorate. More sodium carbonate was added to the iron-containing solution to increase its pH to 4, precipitating a polyvanadate containing iron and sodium. This precipitate was filtered and treated

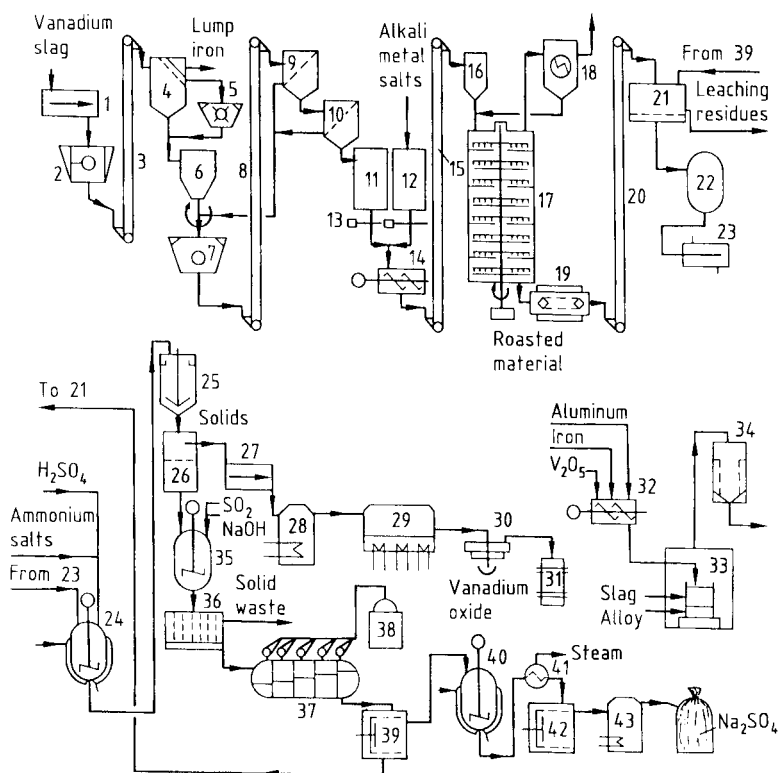


Figure 2. Production of vanadium from vanadium slags: process of the Gesellschaft für Elektrometallurgie
 1) Push feeder; 2) Jaw crusher; 3) Bucket conveyor; 4) Screen; 5) Impact mill; 6) Container with discharge device; 7) Mill; 8) Bucket conveyor; 9) Screen; 10) Air classifier; 11) Container for ground material; 12) Container for alkali metal salt; 13) Metering weighing machine; 14) Mixer; 15) Bucket conveyor; 16) Container with discharge device; 17) Multideck furnace; 18) Electrostatic precipitator; 19) Chain conveyor with cooling; 20) Bucket conveyor; 21) Leaching with filtration; 22) Storage container; 23) Double-tube heat exchanger; 24) Precipitation vessel; 25) Thickener; 26) Solids; 27) Thickener; 28) Dryer; 29) Melting furnace; 30) Cooled rotary table; 31) Packing; 32) Mixer; 33) Aluminothermic reaction; 34) Bag filter; 35) Precipitation vessel; 36) Filter press; 37) Cooling with crystallization; 38) Steam generation; 39) Pusher centrifuge; 40) Melting vessel; 41) Heat exchanger; 42) Pusher centrifuge; 43) Dryer

with a solution of an ammonium salt to replace the sodium ions by ammonium ions. It was then dried and converted to V_2O_5 by fusion.

Zinc carbonate was precipitated from the filtrate after the polyvanadate precipitation.

Combination of Pyrometallurgical and Alkaline Hydrometallurgical Methods. This combined process, which is preferred in practice, is used to treat vanadium-containing residues and spent catalysts. (It was formerly also used for V-containing clays, phosphates, and Pb–Zn vanadates.) The vanadium, which is mainly trivalent, is oxidized at high temperature and converted to alkali metal vanadate, which can be leached with water.

The best known process is alkaline roasting, in one version of which the ore is pelletized with sodium carbonate or compacted. After leaching, the solutions are acidified and ammonium salts are added, precipitating the vanadium as polyvanadate, which is then converted to vanadium pentoxide by calcination.

In the treatment of Pb–Zn vanadates, the zinc and lead were first reduced with carbon in the presence of added sodium carbonate in short drum furnaces. The zinc was distilled off and the lead tapped off as molten metal. The vanadium was then present in the alkaline slag in water-soluble form.

Production of Vanadium Pentoxide from Oil Residues and Boiler Ash. Appreciable amounts of vanadium are present in mineral oil, especially Venezuelan and Russian oils. The vanadium accumulates in the soot and ash of oil-fired boilers and in oil distillation residues and is sold in this form by power stations and refineries. These secondary raw materials, which sometimes contain $> 50\%$ V_2O_5 , can be blended in the pyrometallurgical/hydrometallurgical process [13] or treated separately.

The extraction of vanadium from mineral oil combustion residues is gaining in importance, since the asphalt-like oil deposits of the Orinoco basin in Venezuela can now be processed into a fuel resembling mineral oil by emulsification with water with addition of magnesium nitrate. The fuel is used for energy generation in power stations. The amount of vanadium in the resulting boiler ashes is expected to reach the same order of magnitude as is currently generated in vanadium slags.

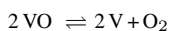
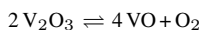
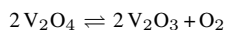
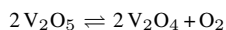
Production of V_2O_5 during the Processing of Bauxites. Some deposits of bauxite contain high levels of vanadium, and during alumina production this ends up in the salt residue, from which V_2O_5 can be obtained. This process is more expensive than vanadium production from slags and causes severe wastewater treatment problems due to the arsenic originating from the raw material [19]. Small amounts of vanadium are obtained by this method in India and Hungary [13].

5. Production of Vanadium, Ferrovandium, and Other Alloys

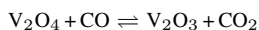
5.1. Reduction Behavior of Vanadium Oxides

The most important oxide obtained on treating raw materials is vanadium pentoxide, V_2O_5 (see Chap. 6).

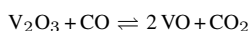
The oxygen partial pressure in equilibrium with the vanadium oxides in accordance with the equations



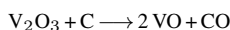
can be calculated from thermodynamic data [20]. The reactions are strongly endothermic, and have positive free enthalpies in the temperature range 298.15–2000 K (Fig. 3). V_2O_5 is the only oxide which dissociates to a large extent, the oxygen pressure reaching 0.08 MPa at 2000 K. In the presence of reducing gases such as CO and H_2 , the higher oxides are reduced to V_2O_3 :



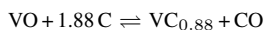
The reduction of V_2O_3 by CO or H_2 in accordance with the equation



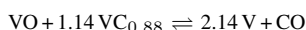
does not go to completion [20], but reduction by carbon is almost complete:



The reaction of VO with carbon initially gives vanadium carbide:



In the further reaction of oxide with carbide,



it can be calculated from thermodynamic data [20] that the CO pressure will reach ca. 600 Pa at 2000 K. However, VO and C are soluble in vanadium at high temperature. This does not favor carbothermic reduction to pure vanadium metal even under high vacuum, and it is difficult to obtain a metal with low C and O contents [1].

For the metallothermic reduction of vanadium oxide silicon, aluminum, calcium, and magnesium could be considered as possible reagents, of which calcium and magnesium have an especially strong reduction potential. However, reduction with aluminum is incomplete, the vanadium produced being either oxygen-containing and low in aluminum, or aluminum-containing and low in oxygen [21], which, in addition, leads to loss of vanadium in the slag. In the production of VAl, a low-oxygen, aluminum-containing alloy is refined in a second stage using a vacuum induction furnace and is adjusted

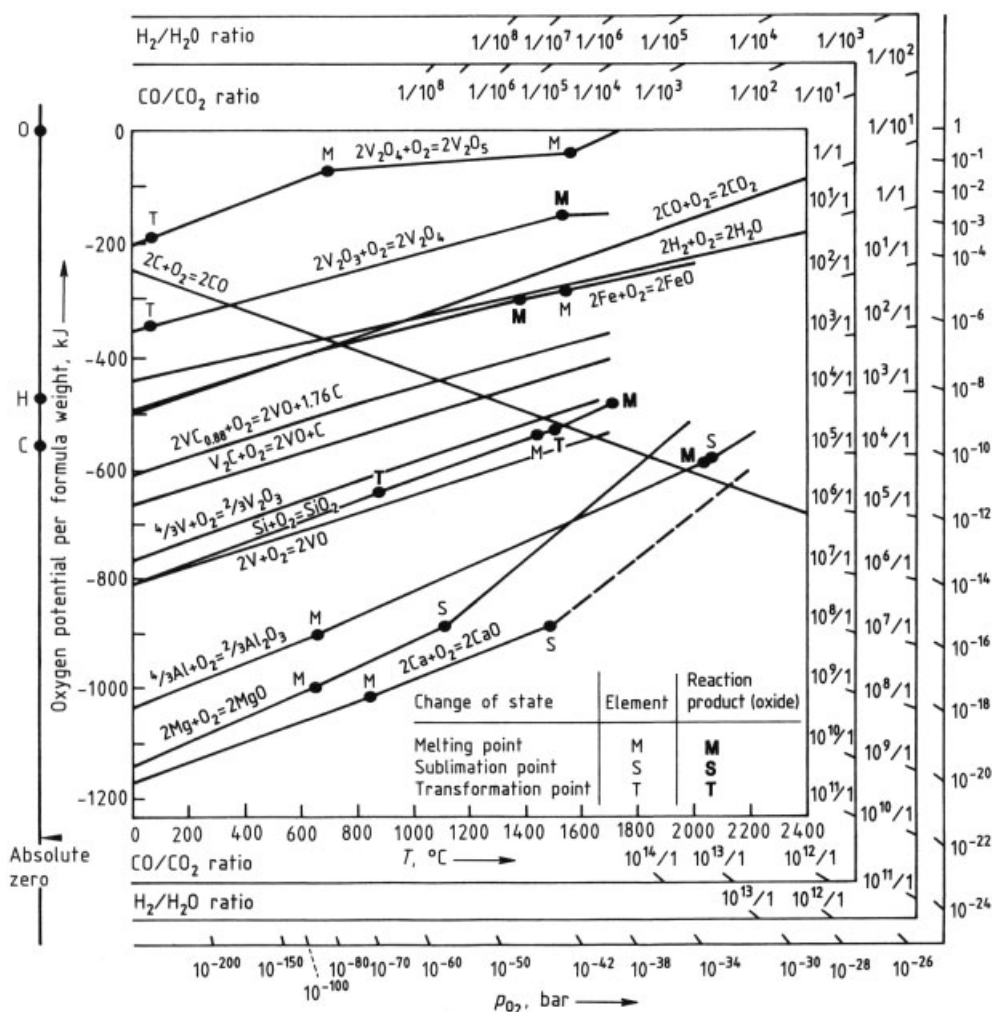


Figure 3. Oxygen potentials of oxides of vanadium and other elements as a function of temperature

to the derived final composition. The refinement of aluminum-free vanadium metal is performed in an electron-beam furnace. The even less complete reduction with silicon is only used in the production of ferrovanadium, as the reaction proceeds better in the presence of iron.

Reduction of the oxides with calcium and magnesium goes almost to completion. As these metals are volatile, it is advantageous to carry out the reaction in closed vessels.

5.2. Production of Vanadium Metal and its Alloys

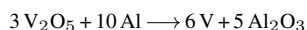
Reduction of Vanadium Oxide with Carbon. Carbothermic reduction of vanadium oxides is possible (Section 4.1), but the vanadium produced is of high oxygen and carbon content; thus, this method is rarely used in practice. Also, the formation of a low-melting ternary eutectic (96.6 % V, 2.8 % C, 0.6 % O; mp 1500 °C) prevents the reaction going to completion [22].

Avoidance of these problems by reducing vanadium oxide with vanadium carbide (carbidothemic production) has been proposed [23], [24]. High-purity vanadium ($> 99.8\%$ V)

can be obtained by multiple sintering (two indirect sintering stages, one direct stage, and post-sintering).

Reduction of V_2O_5 with Calcium. A pressure vessel lined with pure magnesium oxide is used in this process. A mixture of high-purity V_2O_5 , double-distilled calcium chippings, and some high-purity sulfur as a booster is caused to react by heating [25]. This technique leads to a compact metal regulus (8–12 kg, 99.5–99.8 % V) which is well separated from the slag. With a calcium excess of up to 70 %, a vanadium yield of 85–90 % is obtained. The Vickers hardness (HV 10) of this vanadium metal is 80–180, depending on the impurities present (mainly O, N, C, and Si) [1].

Reduction of V_2O_5 or V_2O_3 with Aluminum [26], [27]. The reduction



is self-sustaining (\rightarrow Aluminothermic Processes, Chap. 2.1.), i.e., after initiation it proceeds without additional heating. The metal and slag are melted and separate well from each other. An excess of heat is produced during reduction. For process control, only a fraction of the material is ignited primarily and further material is then charged to the melt. To further decrease the exothermicity, a mixture of V_2O_5 and V_2O_3 is used. In the reduction of V_2O_3 with aluminum, boosters such as $KClO_3$ must be added to increase the reaction heat.

In the process developed by Teledyne Wah Chang Albany [28], a vanadium–aluminum alloy containing 13–15 % Al is obtained by the aluminothermic reaction of high-purity V_2O_5 with aluminum powder in a closed vessel. The steel reaction vessel is lined with aluminum oxide at the bottom and in the reaction zone. After evacuation, it is purged several times with helium, and the charge is then electrically ignited with a heated resistance wire. The metal blocks obtained are refined in an electron-beam furnace by remelting several times. The high aluminum content leads to the removal of most of the oxygen by volatilization of aluminum suboxides, but nitrogen and silicon cannot be removed by this method. A purity of 99.93 % V can be achieved.

In a similar process [29], the metal produced in a closed reactor by the aluminother-

mic method is treated at 1700 °C and 10^{-4} Pa in a resistance-heated vacuum furnace, causing most of the aluminum to volatilize. Further purification by melting in an electron-beam furnace gives 99.93 % pure metal.

Refining. Vanadium–aluminum alloys produced aluminothermically can be refined by molten salt electrolysis (electrorefining) [26]. A metal containing ca. 4.8 % Al, 0.09 % O, and 0.08 % N can be refined by this method to give 99.6 % pure vanadium.

The most effective purification of technically pure vanadium is achieved by the van Arkel process. Vanadium and iodine are heated together in a closed, evacuated tube, forming VI_2 and VI_3 . These are then sublimed and decomposed in a second reaction chamber on a tungsten or vanadium wire heated to 800 °C, yielding a 99.95 % pure vanadium. The equipment required is complex and expensive, and the industrial potential is limited.

Production of Semifinished Products (Sheet, Rods, Tubes, Wire). The cast blocks of vanadium metal and alloys have a coarse structure which must first be converted into a fine-grained structure by extruding or forging at 900–1200 °C and then annealing. To prevent reaction of the vanadium with atmospheric oxygen and nitrogen, the blocks are encased in an iron or stainless steel cladding by vacuum welding. Owing to the good ductility of vanadium, subsequent metal working by rolling, forging, or drawing can be carried out at 100–500 °C. Pure vanadium can normally be formed at room temperature into thin sheets, wires, and tubes.

Vanadium and vanadium alloys can be welded using tungsten electrodes protected by an inert gas (TIG welding). Vanadium can be machined like niobium and tantalum. Excessive heating due to machining at high speeds must be avoided [30], [31].

5.3. Ferrovandium

According to DIN 17 563 [32], ferrovanadium is “a master alloy with a vanadium content of at least 50 wt % produced by reduction of the corresponding raw materials or their concentrates.”

In the United States alloys with lower vanadium contents are also commercially available. The iron–vanadium and vanadium–aluminum master alloys and the commercial grades of vanadium alloys are listed in Table 6.

Table 6. Commercial grades of vanadium master alloys [33], [34]

Ferrovanadium	% V	% C	% Si	% Al
FeV 40	35–48	0.5	2.0	0.5
FeV 50	48–60	0.5	2.0	0.3
FeV 60	50–65	<0.15	<1.5	<2.0
FeV 80	78–82	0.15	1.5	<1.5

The Fe–V phase diagram (Fig. 4) shows almost complete mutual solubility of the elements. At compositions approximating to FeV below 1200 °C, a σ -phase exists which forms tetragonal crystals.

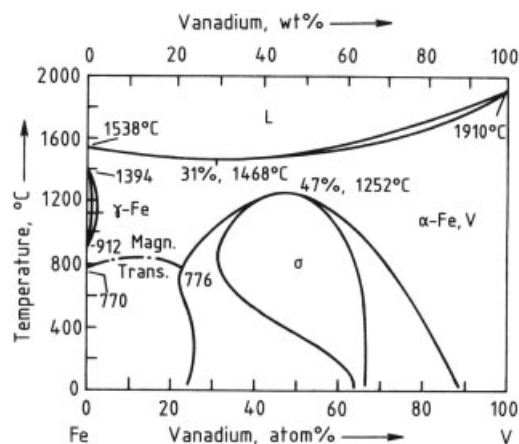


Figure 4. Phase diagram Fe–V [35]

5.3.1. Production from Vanadium Oxides

The reduction of vanadium oxides is assisted by the presence of iron, as the activity of the vanadium is reduced, and the solubility of oxygen in vanadium–iron is much lower than in pure vanadium, because of the lower melting point [21]. The vanadium oxides can therefore be reduced with carbon, silicon, and aluminum in the presence of iron, the product being ferrovanadium.

Reduction with Carbon. The high affinity of vanadium for carbon leads to carbide formation, so that carbothermic reduction can only be

used when there is no requirement for vanadium with low carbon content. The Union Carbide Corporation has developed a process that gives a V_2C -containing alloy known as Carvan [36], with a C content in the range 10–13 % [33].

Reduction with Silicon. Under today's conditions for the processing of V_2O_5 , silicothermic reduction is no longer generally profitable, as the process has multiple stages and gives a poor vanadium yield in the form of a low-vanadium ferrovanadium. The vanadium losses in this process are 10–25 % [37].

Reduction with Aluminum. The high-vanadium grades of ferrovanadium, FeV 60, FeV 80, and FeV 90, are now usually produced by aluminothermic treatment of V_2O_5 . The aluminothermic process can readily be controlled on a large scale. It is especially suitable for the treatment of vanadium pentoxide because it gives a high yield of high-grade ferrovanadium in a single process step.

After ignition, the reaction of V_2O_5 with aluminum is self-sustaining. Some of the mixture of V_2O_5 flakes, aluminum powder or granules, fine steel shot, and an initiating mixture (e.g., BaO_2 + Al powder) is ignited, and further quantities of the mixture are then added. The combustion time for the usual batch size (to produce 0.5–1 t metal) is only a few minutes. After cooling for 2–3 d, the furnace is dismantled, and the block of metal at the bottom is cleaned and crushed or ground to the commercially desired particle size.

As the reaction proceeds very rapidly, the aluminum in the metal and the vanadium oxide in the slag may not attain equilibrium, so that the vanadium content of the slag may be too high. To prevent this, an electric arc is ignited after completion of the aluminothermic reaction to maintain the molten state of the melt and the slag until reaction is complete [38].

5.3.2. Direct Production from Slags and Residues

Enriched vanadium-containing oxidation slags (see Chap. 4) can also be processed directly to a technical-grade ferrovanadium. In the method

of Christiania Spigerverk [39], a 50 % ferrovanadium is obtained in an electric arc furnace by a two-stage reduction process. In the first stage, the FeO fraction of the slag is reduced with ferrosilicon (FeSi 75) with addition of lime, and in the second stage the slag obtained in the first stage is reduced with 90 % silicon to give a ferrovanadium alloy. The vanadium yield is 80 %, and the FeV still contains traces of Si, Cr, Mn and Ti.

Ferrovanadium can be obtained by the electrosilicothermic treatment of high-vanadium boiler ashes and enriched fly ash, either alone or in combination with vanadium-containing oxidation slags, depending on their composition. As oil residues and fly ash contain only small amounts of iron, the iron removal stage normally necessary with oxidation slags can be omitted.

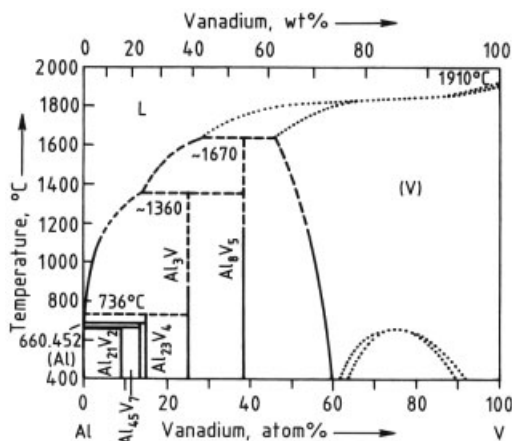


Figure 5. Phase diagram Al–V [35]

5.4. Production of Other Vanadium Master Alloys

Vanadium–Aluminum Master Alloys. In the production of vanadium-containing titanium alloys, especially TiAl6V4, the vanadium is added as a vanadium–aluminum alloy. The Al–V phase diagram (Fig. 5) shows a higher solubility of aluminum on the vanadium-rich side. This results in a wide range of composition in which vanadium–aluminum alloys can be produced:

VAI 40/60	38–42 % V
VAI 50/50	45–54 % V
VAI 65/35	60–65 % V
VAI 80/20	78–82 % V
VAI 85/15	83–87 % V

Vanadium–aluminum alloys are produced aluminothermically. The excess heat produced in this self-sustaining reaction is controlled by slow charging of the reaction mixture. The vanadium–aluminum alloys have a lower density than vanadium (6.11 g/cm³). The melting points of the alloys decrease with increasing aluminum content:

	Density, g/cm ³	Melting range, °C
VAI 80/20 (85 % V)	5.2	1850–1870
VAI 40/60 (40 % V)	3.8	1360–1520

Because of the small difference between the density of the metal and the slag, poor separation or inclusions of slag in the metal can occur in the aluminothermic process. As titanium alloys are used in highly stressed machinery and equipment, the master alloys used are subject to strict quality control and must be free of oxidic inclusions and impurities, especially heavy metals.

Vanadium–aluminum master alloys can also be produced in water-cooled copper molds, preventing contamination by impurities from slag and refractory oxides in the furnace lining [40]. However, the higher cooling rate can lead to inclusion of process slags.

Nitrogen-Containing Vanadium Master Alloys. As vanadium is a strong nitride former, vanadium-containing alloying agents can be nitrated and used for alloying steels with vanadium and nitrogen (see Chap. 5). Examples of nitrogen-containing alloys are ferrovanadium–nitrogen and manganese–vanadium–nitrogen [41].

Other commercial alloys are listed in the following:

VAIFe	69 % V, 19 % Al, 12 % Fe
VAISn	43 % V, 43 % Al, 14 % Sn
VCrAl	50 % V, 40 % Cr, 10 % Al
VCo	50 % V, 50 % Co
VNi	65 % V, 35 % Ni
VMoAl	50–54 % V, 26 % Mo, 22 % Al

6. Uses

Vanadium is mainly used as an alloying element in the steel industry, other major areas of use are [42], [43]

Steel	ca. 85 %
Nonferrous alloys	ca. 9 %
Chemical industry	ca. 4 %
Others	ca. 2 %

The second largest use area is in nonferrous alloys, mostly vanadium-containing titanium alloys and nickel-based superalloys for the aerospace industry. Additional uses are in vanadium-containing alloys for batteries and in grain refining of aluminum alloys. Vanadium compounds, principally the oxidation catalyst V_2O_5 , account for only ca. 3 % of vanadium consumption [12].

Addition to Steel. Vanadium is added to steel mainly as ferrovanadium; technical vanadium carbide and vanadium carbonitride are also used. For the simultaneous addition of vanadium and nitrogen, nitrogen-containing Fe–V alloys are available.

Even small additions of vanadium increase the tensile strength and high-temperature strength of carbon steel [1], [56], and it has a grain refining and dispersion hardening effect in tempering steels.

Addition to Titanium. Alloying with vanadium improves the properties of titanium. The most important alloy is TiAl6V4, which has good strength properties at room temperature and good creep resistance. It is mainly used as a wrought alloy and casting alloy in airframe construction for load-bearing components and fixing devices, and in compressor disks and blades in jet engines. Other areas of increasing importance include power stations, shipbuilding, and reactor technology [13]. Other vanadium-containing titanium alloys with similar strength properties to TiAl6V4 include TiAl3–V2.5, TiV15Cr3Sn3Al3, TiV10Fe2Al3, TiAl6V6Sn2, as well as TiV13Cr11Al3 [44], [45].

In light, corrosion-resistant titanium aluminides (intermetallic γ -TiAl phase) with high-temperature strength, small amounts of vanadium (as well as of chromium and manganese)

increase ductility at room temperature, which is an important criterion for usability and workability of this otherwise brittle material [46].

Other Uses. *Alloys for Batteries.* Intermetallic phases of the ZrV_2 type (Laves phases), in which vanadium is substituted partially by, e.g., Ni, Cr, Ti, or Mn, are used as electrode materials in metal hydride/nickel hydroxide batteries [47].

Coating materials containing vanadium and vanadium compounds are used in the electronics and glass industries as well as for wear protection.

Gettering materials based on Zr–V–Mn or Zr–V–Fe alloys are used for gas purification and for improving vacuums. The main component of these alloys, which contain up to 30 % vanadium, is zirconium [48]. Gettering materials are specially adapted to individual applications; thus, with the exception of some products of the company SAES Getters, only a few standard alloys are marketed.

Vanadium Metal and Alloys. The use of vanadium as a principal component of alloys is in its infancy. As vanadium has higher thermal conductivity and strength and lower thermal expansion and density than stainless steel [49], it has been considered for cladding nuclear fuels for sodium-cooled fast breeder reactors, in the form of either pure metal or an alloy. In the United States, in the late 1960s, a large-scale development program on vanadium alloys was undertaken by the Atomic Energy Division at Westinghouse. Wide-ranging cooperative research projects in the Federal Republic of Germany in 1964–1971 are reported in [31], [50], [51]. A comprehensive review of these developments can be found in [7].

Of the vanadium alloys investigated, those in which titanium, niobium, chromium, and zirconium are the alloying elements seem the most promising.

The behavior of vanadium and its alloys in contact with lithium and sodium is described in [11], [51]. The effect of irradiation by neutrons on the strength properties of vanadium and its alloys is described in [52].

A further possible application of vanadium is in superconductivity. Vanadium–gallium alloys with composition V_3Ga are well known, but

vanadium–niobium alloys containing 30 % Nb and vanadium–hafnium/zirconium alloys also have good superconducting properties.

7. Vanadium Compounds

A large variety of vanadium compounds are used industrially: halides, oxides, nitrates, carbides, silicides, hydrides, vanadates, and organometallics.

Vanadium Oxides. *Vanadium pentoxide* [1314-62-1], V_2O_5 , M_r 181.88, mp 690 °C, ρ 3.36 g/cm³, heat of formation ΔH^{298} –1550.8 kJ/mol, is orange yellow in color and is traded as fused flakes or powder. Reaction with alkali metal hydroxides or ammonium hydroxide gives vanadates. V_2O_5 is prepared by thermal decomposition of ammonium vanadates at 500–600 °C in an oxidizing atmosphere (air). It is by far the most important vanadium compound. V_2O_5 is used as an oxidation catalyst in heterogeneous and homogeneous catalytic processes for the production of sulfuric acid from SO_2 , phthalic anhydride from naphthalene or *o*-xylene, maleic anhydride from benzene or *n*-butane/butene, adipic acid from cyclohexanol/cyclohexanone, and acrylic acid from propane. Minor amounts are used in the production of oxalic acid from cellulose and of anthraquinone from anthracene.

V_2O_5 is used to lower the melting point of enamel frits for the coating of aluminum substrates. FeV and VAl master alloys are preferably produced from V_2O_5 fused flakes due to the low loss on ignition, low sulfur and dust contents, and high density of the molten oxide compared to powder.

Further uses of V_2O_5 are as a corrosion inhibitor in the CO_2 scrubbing solutions of the Benfield and related processes for the production of hydrogen from hydrocarbons, as cathode in primary and secondary (rechargeable) lithium batteries, as UV absorbent in glass, in YVO_4 : Eu^{3+} red phosphors for high-pressure mercury lamps and TV screens, for glazes [53], for yellow (SnO_2/V_2O_5) and blue (ZrO_2/V_2O_5) pigments [13], as colloidal solution for antistatic layers on photographic material [54], and as a starting material for the production of carbides, nitrides,

carbonitrides, silicides, halides, vanadates, and vanadium salts.

Vanadium trioxide [1314-34-7], V_2O_3 , M_r 149.88, mp 1977 °C, ρ 4.99 g/cm³, heat of formation ΔH^{298} –1218.8 kJ/mol, black powder, is formed by thermal decomposition of ammonium vanadates at 600–900 °C in a reducing atmosphere (H_2 , CO, CH_4 , NH_3). The most important application is as an alternative to V_2O_5 in the production of FeV, VAl master alloys, high-purity vanadium metal, and vanadium carbides and carbonitrides [55].

Vanadium suboxides such as V_2O_4 [12036-21-4], M_r 82.94, mp 1642 °C, heat of formation ΔH^{298} –1427.37 kJ/mol, dark blue in color, or V_6O_{13} [11099-11-9], M_r 513.64, colored bluish black, are of minor industrial importance [56]. They are produced by heating stoichiometric mixtures of vanadium oxides or by reduction of ammonium vanadates or V_2O_5 in atmospheres of controlled reduction potential. Bronzes of V_6O_{13} or V_5O_{11} with Li_2O are used for lithium ion batteries.

Vanadates. The most important product is *ammonium metavanadate* [7803-55-6], NH_4VO_3 , M_r 116.98, heat of formation ΔH^{298} –1551.0 kJ/mol, a white powder. Thermal decomposition starts at 70 °C. It is sparingly soluble in cold water (ca. 1 %), but readily soluble in mono- and diethanolamine. It is precipitated from neutral alkali metal vanadate solutions by the addition of ammonium chloride or ammonium sulfate. Because of its ready conversion to V_2O_5 at elevated temperatures in oxidizing atmospheres, it is used as a substitute in the production of, e.g., DENOX catalysts and zirconium vanadium oxide yellow ceramic colorants.

Ammonium polyvanadate [11115-67-6], $(NH_4)_2V_6O_{16}$, M_r 597.72, is an orange powder, produced by the addition of mineral acids and ammonium salts to alkali metal vanadates at pH 2–3 [57]. It is an intermediate product in the production of vanadium pentoxide.

Sodium ammonium vanadate [39455-80-6], $2(NH_4)_2O \cdot Na_2O \cdot 5V_2O_5 \cdot 15H_2O$, M_r 1345.77, an orange powder, is precipitated from sodium vanadate solutions by the addition of ammonium salts at pH 5–6. It is almost exclusively used as a soluble oxidation catalyst for the desulfurization of H_2S -containing gases by the Stretford process.

Sodium metavanadate [13718-26-8], NaVO_3 , M_r 121.93 and *potassium metavanadate* [13769-43-2], KVO_3 , M_r 138.04, both white powders, are water-soluble compounds. They are added as corrosion inhibitors to CO_2 washing solutions in the production of H_2 from hydrocarbons.

Vanadium Salts. *Vanadyl sulfate* [27774-13-6], $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, M_r 253.08, is produced by the reaction of V_2O_5 and SO_2 in aqueous media, and forms blue, water-soluble crystals. It is used in catalyst production as alternative to V_2O_5 . In multivitamin/multimineral pills it is the active component for fast energy supply to the muscles by enhancing glucose metabolism in the blood. It acts as an orally applied insulin mimic.

VOSO_4 , of blue color, and $\text{V}_2(\text{SO}_4)_3$, of green color, are the feed solutions for the vanadium redox battery. This battery contains vanadium(V) (yellow) and vanadium(II) (pink) in dilute sulfuric acid as electrodes when charged [58].

Vanadyl oxalate [14974-48-2], VOC_2O_4 , M_r 154.96, forms blue, water-soluble crystals and is used in catalyst production as alternative to vanadates and vanadium oxides.

Vanadium Halides. Only *vanadium oxytrichloride* [7727-18-6], VOCl_3 , M_r 173.30, mp -79.5°C , bp 126.7°C , ρ 1.82 g/cm^3 , a bright yellow liquid, *vanadium tetrachloride* [7632-51-1], VCl_4 , M_r 192.75, bp 148°C , a red brown liquid, and *vanadium trichloride* [7718-98-1], VCl_3 , M_r 157.30, boiling range 300 – 400°C (disproportionates), a deep purple solid, are of commercial interest. Whereas VOCl_3 is stable, VCl_4 slowly decomposes into solid VCl_3 and Cl_2 . VOCl_3 is produced by the reaction of V_2O_5 and carbon with chlorine gas. For the production of VCl_4 , oxygen-free vanadium compounds such as vanadium carbide or vanadium carbonitride are reacted with chlorine gas. The chlorides are used as catalysts in the production of EPDM (ethylene–propene–diene) rubber and polyethylene and are starting materials [59] for the preparation of organic vanadium compounds.

Organic Vanadium Compounds. Representatives of this class are vanadium(IV) and

vanadium(III) acetylacetonates, naphthenates, octoates, and alkoxides (iso/*n*-butyl, iso/*n*-propyl), which are soluble in organic solvents. They are used in siccatives, antifouling paints, as catalysts for stereospecific organic synthesis, and in chemical vapor deposition (CVD).

Vanadium Carbides [12070-10-9]. The monocarbide, VC, has a theoretical carbon content of 19.08 % and melts at 2830°C . It has a wide phase range. VC is isomorphous with VO and VN. Pure VC can be prepared by carburizing vanadium hydride powder with carbon in a vacuum [60]. Reaction at 800°C leads to vanadium carbide in which $\text{C} : \text{V} = 0.72$ – 0.87 .

Industrial-grade VC is produced by heating V_2O_5 or V_2O_3 with carbon at 1100°C under a protective atmosphere of hydrogen [61], or by reacting V_2O_3 with carbon in a carbon-tube furnace. The crude carbide formed in the first stage is recarburized at 1700 – 2200°C under vacuum. The final product contains 18.5–19 % total-C and up to 0.5 % free carbon. The VC is not completely free of oxygen because of its isomorphism with VO. VC is added to hard metals in amounts of 0.3–0.5 %. It acts as a grain growth limiter [3]. Another carbide, V_2C , with a theoretical carbon content of 10.54 %, also exists. This also has a large range of homogeneity, and decomposes at 1850°C . It is of no industrial importance as such, but is formed in all carbon-containing vanadium alloys.

Vanadium Nitrides [24646-85-3]. Three nitrides exist: VN, V_2N , and V_3N . The mononitride, mp 2350°C , is a grayish-brown powder, isomorphous with VC and VO [62]. Its theoretical composition is 78.45 % V, 21.55 % N, but its range of homogeneity extends from $\text{VN}_{1.0}$ to $\text{VN}_{0.71}$. It can be obtained by the reaction of vanadium tetrachloride with mixtures of nitrogen and hydrogen gas, using the technique of growth on tungsten wires at 1400 – 1600°C . Although the preparation of VN from vanadium oxides is difficult because of the isomorphism mentioned above, a product containing 78.3 % V, 21.1 % N, and 0.5 % O can be obtained by reduction with carbon in an atmosphere of nitrogen [61].

As vanadium carbides and nitrides are mutually soluble, vanadium carbonitrides with a wide range of $\text{C} : \text{N}$ ratios can be prepared at

1100–1400 °C. This is true for both V(C,N) and V₂(C,N). Two broad three-phase regions extend continuously between the corresponding phases VC–VN and V₂C–V₂N.

Vanadium Silicides [12039-87-1]. VSi₂, *mp* 1650 °C, can be prepared by sinter metallurgy. For example, the pure substance can be prepared by exothermic reaction sintering of vanadium and silicon powder [63]. In industry, it is obtained by the reaction of vanadium oxides with SiO₂ and carbon (or with SiC) at 1200–1800 °C under vacuum.

Vanadium Hydrides [13966-93-3]. In the H–V system [64] the following phases occur: β₁, corresponding to ca. V₂H (low temperature), 33 atom % H; β₂, corresponding to V₂H or VH, 33–50 atom % H; δ, corresponding to V₃H₂, 40 atom % H; γ, corresponding to VH₂, 66.7 atom % H.

8. Analysis

The most important analysis is the determination of vanadium in raw materials, especially vanadium-containing slags and the commercial products vanadium oxide and ferrovandium [65].

To determine vanadium in raw materials, the sample is fused with sodium peroxide and sodium carbonate, the solidified product is leached with water, and the vanadium-containing solution so obtained is acidified with sulfuric acid. The vanadium is completely oxidized with potassium manganate(VII) to the pentavalent state, and the solution is back-titrated with iron(II) sulfate, with diphenylamine as indicator.

In the analysis of vanadium oxide, the sample is dissolved in sulfuric acid, completely reduced with iron(II) sulfate to the tetravalent state, and back-titrated potentiometrically with potassium manganate(VII) solution, using a calomel reference electrode.

Ferrovandium is also analyzed potentiometrically. The sample is dissolved in sulfuric/nitric acid, and is then oxidized by potassium manganate(VII). The vanadium, now in pentavalent form, is reduced with iron(II) solution, and potentiometrically back-titrated with potassium manganate(VII) solution, using a calomel reference electrode.

9. Economic Aspects

Consumption, Production Capacity, and Prices. The development of vanadium market prices is governed by consumer demand and existing production capacities. For main uses of vanadium and their shares see Chapter 6. The dependence of vanadium production on world steel production is shown in Figure 6 [66]. Total world demand is compared to available production capacities in Figure 7 [67]. This led to the price trend shown in Figure 8 [67].

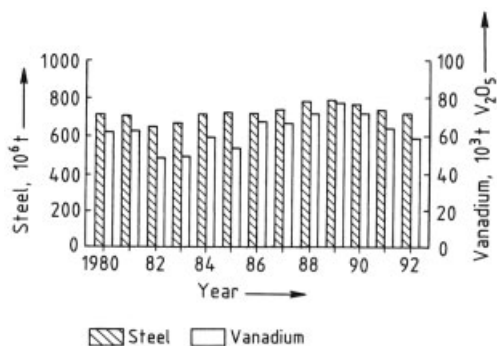


Figure 6. World production of steel and vanadium

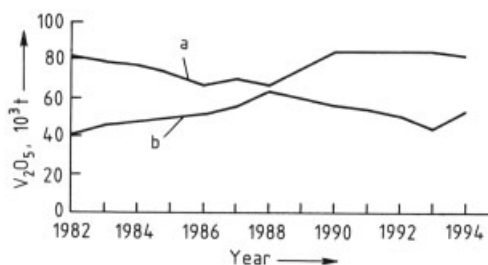


Figure 7. Worldwide vanadium capacity (a) and demand (b)

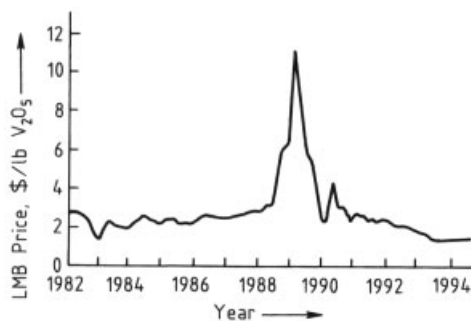


Figure 8. Vanadium price trends

For the vanadium demand of the western world, South Africa is the major exporter (Table 7). Vanadium in the form of slag and oxides was traded to converters in Europe, Japan, and the United States, for the production of ferrovanadium. Since 1994 most South African suppliers have installed their own ferrovanadium production capacity. This will eventually lead to the nonavailability of South African preproducts for the converters mentioned above. Their plants will have to use other raw materials, such as residues from mineral oil processing, or cease production.

Further suppliers of vanadium oxides are Russia, whose share for export strongly depends on its own economic development; and China, which is expected to turn from an exporter to an importer because of its high economic growth rate.

Ferrovanadium producers are listed in the following [61]:

Country	Company
Argentina	Pamet Stein Ferroaleaciones Sacifa
Austria	Treibacher Industrie AG
Belgium	SADACI NV
Brazil	Termoligas Metalurgicas SA Cia Paulista de Ferro Ligas
Canada	Masteralloy Products Inc. Panzihua Iron and Steel Plant
China	Emei Ferroalloy Plant Jinzhou Ferroalloy plant
Czech Republic	Nikom Ferroalloy Plant
Germany	GfE Gesellschaft für Elektrometallurgie
Hungary	Ötvözetgyar; Hungaraloy
India	Birla
Japan	Awamura Metal Industry Co. Ltd. Taiyo Mining and Industrial Co. NKK Corp.
Mexico	Ferroaleaciones de Mexico FERROMEX Ferralver SA
CIS	Chusovskoy Metallurgical Kombinat Tulachermet Kombinat
Spain	Ferroaleaciones Especiales Asturias
South Africa	Highveld Steel and Vanadium Corp. Ltd. Vametco Vantech
United States	BEAR Metallurgical Corp. Shieldalloy Corp. Strategic Metal Corp., Stratcor

10. Environmental Protection and Toxicology

Soil. In sulfidic and oxidized form, vanadium is a ubiquitous element with an average abundance of 150 mg/kg in the earth's crust. The concentrations vary widely, between a few ppm and 1000 ppm. Depending on geological conditions, even higher values can be found, e.g., 1650 ppm vanadium in oil shales of permian copper schist [68]. The vanadium content of oil shale and mineral oil, in which it is present primarily as porphyrin complexes, is due to biological processes. Higher anthropogenic burdens can be found only in a few isolated geographic locations. In the upper layers of arable soils utilization of mineral fertilizers leads to accumulation of vanadium, which is retained and is only slightly mobile [69].

Air. Vanadium concentrations in uncontaminated air can reach 1 ng/m^3 , caused by whirled-up dust from weathered rock and by evaporation of water droplets driven off of surface waters by wind and waves. Increased concentrations are recorded mainly in urban areas. They originate mainly from combustion of coal and especially heavy fuel oil. Concentrations of ca. $10\text{--}35 \text{ ng/m}^3$ measured in the past (maximum values of up to 1000 ppm, recorded in London, 1962) are lower today, due to the use of efficient waste air purification systems. Industrial activities are of only minor, local importance in the pollution of the air with vanadium.

Water. Vanadium dissolved in water is present almost exclusively in the pentavalent form. In running waters, its concentration range is ca. $0.1\text{--}220 \mu\text{g/L}$ [70], the vanadium concentration in the water correlates to these in rocks near the river source in the river bed. The sediment of creeks also mirrors the abundance in the surrounding area. Seawater contains $0.3\text{--}29 \mu\text{g/L}$ vanadium [70]. Accumulation does not occur, since the vanadium input from running waters is transferred to the sediment by precipitation and biochemical processes.

Water contamination by vanadium takes place only to a minor extent. For removing vanadium from wastewater, single- or multiple-stage precipitation with iron or lime is employed.

Table 7. World exports of vanadium, 1989–1992 [66] (in tonnes of V_2O_5)

Country	Exports				
	1989	1990	1991	1992	%
South Africa ^a	32 950	25 989	25 561	24 000	84.7
New Zealand ^b	2 000	4 000	4 500	3 000	10.6
CIS	1 500	1 350	1 200	1 200	4.2
Others ^c	200	150	150	150	0.5
Total world	36 650	31 489	31 411	28 350	100

^a Including Republic of South Africa and Bophuthatswana.^b Estimates.^c China is considered to be a net importer of vanadium at present. Its re-exports are, therefore, not shown in this table.**Table 8.** Toxicological data [78], [79]

	Oral LD ₅₀ (14 d), mg/kg body weight	Inhalative LC ₅₀ (14 d), mg/L	Dermal LD ₅₀ (14 d), mg/kg body weight
V ₂ O ₅ , analytical grade	470 (male) 467 (female)	11.09 (male) 4.3 (female)	>2500 (male) >2500 (female)
V ₂ O ₃ , technical grade	8713 (male) 5639 (female)	>6.65 (male) >6.65 (female)	>2500 (male) >2500 (female)
Ammonium metavanadate	218 (male) 141 (female)	2.61 (male) 2.43 (female)	>2500 (male) >2500 (female)
Potassium metavanadate	318 (male) 314 (female)	1.85 (male) 4.16 (female)	>2500 (male) >2500 (female)
BiVO ₄ – BiMoO ₄	>5000	>5.15	

Fauna and Flora. Vanadium is considered to be essential for a number of organisms [71–73]. In vertebrates the average concentration is 0.1 mg vanadium per kg dry matter. Considerably higher concentrations (≤ 0.1 g/kg) can be found in lower organisms. Especially in one order of invertebrates (ascidians), vanadium accumulates in unusually high amounts [74]. In some species of these organisms, the vanadium is present in green blood cells (vanadocytes) and is complexed by pyrrole rings [75]. Data on vanadium concentrations in humans vary widely, between 100 μ g [76] and 17–43 mg [77]. Fat tissue, bones, teeth, bone marrow, as well as serum are especially rich in vanadium.

In general, the vanadium concentration in plants is related to that in the soil. As with animals, plants vary widely in vanadium content. For example, in fly agaric (*Amanita muscaria*) concentrations 100-times as high as in other fungi are found, independent of location. The reasons for this are not yet known [74].

Toxicology. Toxicity data for some vanadium compounds are given in Table 8. The data show a correlation of toxicity with oxidation state and solubility. Toxicity decreases with de-

creasing oxidation state and decreasing solubility.

In investigations of neurobehavioral, neuropsychological, psychosomatic, and psychological parameters as a function of exposure to V₂O₅ in dust among workers in an industrial plant, no significant changes compared to uncontaminated persons were found, independent of the concentration of vanadium pentoxide [80].

Occupational Safety. For vanadium pentoxide, there is a total dust limit value (0.5 mg/m³) and a limit value for fine dust (0.05 mg/m³); in Germany, the definition of the latter is based on studies on volunteers [81].

11. References

1. R. Kieffer, G. Jangg, P. Ettmayer: *Sondermetalle*, Springer Verlag, Wien 1971.
2. A. M. Sage: "Discovery and History of Vanadium and its Contribution to Life in the Modern World," Metals Society, 1981.
3. R. Kieffer, H. Braun: *Vanadium, Niob, Tantal*, Springer Verlag, Berlin 1963.
4. W. Rostocker: *The Metallurgy of Vanadium*, Wiley, Chapman & Hall, New York 1958.

5. *Bull. Alloy Phase Diagrams* **2** (1981) no. 1, 40–41, 146; **2** (1981) no. 2, 172.
6. I. Barin, O. Knacke: *Thermochemical Properties of Inorganic Substances*, Springer Verlag, Berlin, Verlag Stahleisen, Düsseldorf 1973.
7. D. L. Harrod, R. E. Gold, *Int. Met. Rev.* **25** (1980) 163–221.
8. E. Fromm, E. Gebhardt: *Gase und Kohlenstoff in Metallen*, Springer Verlag, Berlin 1976.
9. H. E. Dunn, D. L. Edlung: “Vanadium”, in C. A. Hampel (ed.): *Rare Metals Handbook*, 2nd ed., Reinhold, Chapman & Hall, London 1961, pp. 640–642.
10. D. Schlain, C. B. Kenenhan, W. L. Ackermann, *J. Less-Common Met.* **3** (1961) 458–467.
11. R. L. Ammon, *Int. et. Rev.* **25** (1980) 255–268.
12. M. Rühle, *Metall (Berlin)* **35** (1981) 1168–1172, 1282–1285.
13. Bundesanstalt für Geowissenschaften und Rohstoffe: *Untersuchungen über Angebot und Nachfrage mineralischer Rohstoffe, XIV. Vanadium*, Berlin – Hannover 1981.
14. P. Storm: “Vanadium – Sources, Applications, and Markets,” *Raw Materials Report*, **vol. 10, no. 3**, Royal Institute of Technology, Stockholm.
15. R. K. Evans: Vanitec, reprint from *Met. Mater.*, April 1978.
16. B. Rohrmann, A. G. Raper, *J. Iron Steel Inst. London* 1970, April, 336–341.
17. Ullmann, 3rd ed., **18**, 56.
18. L. White, *Eng. Min. J.* **177** (1976) Jan., 87–91.
19. H.-J. Retelsdorf, *Metall (Berlin)* **35** (1981) 1166–1167.
20. A. D. Mah: “Thermodynamic Properties of Vanadium and its Compounds,” *Bur. Mines Rep. Invest.* **6727** (1966).
21. W. Schmidt: “Untersuchungen an Vanadiummetall und seinen aluminothermisch hergestellten Legierungen mit Aluminium und Eisen,” Ph.D. Thesis, RWTH Aachen 1969.
22. M. F. Joly: *2nd United Nations Int. Conf. on the Peaceful Use of Atomic Energy*, Geneve, May 1958, Paper No. A/Cnf. 15/P/1274.
23. R. Kiefer, H. Bach, H. Lutz, *Metall (Berlin)* **21** (1967) 19–22.
24. R. Kiefer, F. Lihl, E. Effenberger, *Z. Metallk.* **60** (1969) 94–100.
25. T. T. Campbell, F. E. Block, E. R. Anderson: “Reducing Vanadium Compounds in Bomb Reactors,” *Bur. Mines Rep. Invest.* **6374** (1964).
26. P. V. S. Pillai, K. U. Nair, T. K. Mukherjee, C. K. Gupta, *Trans. Indian Inst. Met.* **26** (1973) no. 6, 24–30.
27. T. K. Mukherjee, C. K. Gupta, *J. Less-Common Met.* **27** (1972) 251 ff.
28. C. T. Wang, E. F. Baroch, S. A. Worcester, Y. S. Shen, *Met. Trans.* **1** (1970) no. 6, 1683–1689.
29. O. N. Carlson, H. R. Burkholder, G. A. Martsching, F. A. Schmidt: *Extractive Metallurgy Refractory Metals Proc. Symp.* 1981, pp. 191–203.
30. R. W. Buckmann, Jr., *Int. Met. Rev.* **25** (1980) 158–162.
31. M. Rühle, *Metall (Berlin)* **33** (1979) 140–147.
32. DIN 17 563 Ferrovanadium, Technische Lieferbedingungen, Dec. 1965.
33. G. Roethe, W. Gocht: *Handbuch der Metallmärkte*, Springer Verlag, Berlin 1974.
34. GfE Gesellschaft für Elektrometallurgie mbH, company brochure Nürnberg, Aug., 94.
35. J. F. Smith: *Phase Diagrams of Binary Vanadium Alloys*, American Society for Metals Int., Met. Park, Ohio 1989.
36. UCC, US 3 334 992, 1962.
37. O. Smetana: “Ferrovanadin und Vanadinmetall,” in *Durrer-Volkert: Metallurgie der Ferrolegierungen*, 2nd ed., Springer Verlag, Berlin 1972.
38. F. Goebel, OE 169 315, 1951.
39. Christiania Spigerverk, NO 115 556, 1967.
40. F. H. Perfect, *Trans. Metall. Soc. AIME* **239** (1967) 1282–1286.
41. Ges. f. Elektrometallurgie, DE 1 558 500, 1967.
42. R. Hähn: “Vanadin-Gewinnung und Verwendung,” *Erzmetall* **40** (1987) no. 6, 298 ff.
43. O. E. Kraus, *Stahl Eisen* **109** (1989) no. 11, 547–552.
44. H. B. Bomberger, F. H. Froes, P. H. Morton: “Titanium – A Historical Perspective, Titanium Technology: Present Status and Future Trends,” *Tit. Dev. Ass.* 1985.
45. K. Rüdiger, *DVS-Ber.* **53** (1978) 39–47.
46. Y.-W. Kim, *J. Met.* **46** (1994) no. 7, 30.
47. A. Züttel, F. Meli, L. Schlapbach, *Z. Phys. Chem. (Munich)* **183** (1994) 355.
48. K. Ichimura, M. Matsuyama, K. Watanabe, *J. Vac. Sci. Technol. A* **5** (1985) no. 2, 3–4.
49. F. L. Yaggee, E. R. Gilbert, J. W. Styles, *J. Less-Common Met.* **19** (1969) 39–51.
50. M. Schirra, *Metall (Berlin)* **33** (1979) 455–465.
51. H. U. Borgstedt, *Metall (Berlin)* **33** (1979) 264–266.

52. R. E. Gold, D. L. Harrod, *Int. Met. Rev.* **25** (1980) 232–254.
53. *Nachr. Chem. Tech.* **16** (1968) no. 2, 23.
54. Eastman Kodak, FR 7 522 060, 1975.
55. R. Hähn: Dissertation, RWTH Aachen 1983.
56. Combustion Engineering, US 4 486 400, 1984.
57. U. M. Levanto, *Acta Polytech. Scand. Chem. Technol. Metall. Ser.* **82** (1969) 37.
58. M. Skyllaskazacos et al.: “Characteristics and Performance of 1 kW UNSW Vanadium Redox Battery” *J. Power Sources* **35** (1991) 399–404.
59. Akzo Chemicals Inc.: “Polymerization Catalysts,” Bulletin 92-03, 1992.
60. G. V. Samsonov, V. Ya. Vanmanko, L. N. Okhremchuk, B. M. Rud, *Izv. Akad. Nauk SSSR Neorg. Mater* **10** (1974) no. 1, 52–56; *Chem. Abstr.* **80** (1974) 90 458.
61. R. Kieffer, F. Benesovski: *Hartstoffe*, Springer Verlag, Wien 1963.
62. P. Ettmayer, R. Kieffer, F. Hattinger, *Metall (Berlin)* **28** (1974) 1151–1156.
63. F. Binder, *Radex Rundsch.* 1975, no. 4, 539–540.
64. J. F. Smith, D. T. Peterson, *Bull. Alloy Phase Diagrams* **3** (1982) no. 1, 55–60.
65. Chemiker-Ausschuß: *Analyse der Metalle*, vol. 1: Schiedsanalysen, vol. 2: Betriebsanalysen, Springer Verlag, Berlin 1961.
66. G. Grohmann: *World Vanadium Review*, Report R 14/93, Rep. of South Africa, Department of Mineral and Energy Affairs.
67. W. Beattie: “Overview of Vanadium and Tungsten Commodity Markets,” *Metals Week Presentation*, reprint, 19th Sept. 1994.
68. H. Fauth, R. Hindel, U. Siewers, J. Zinner: *Geochemischer Atlas Bundesrepublik Deutschland*, Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover 1985.
69. R. Schnabel, C. Koch, C. Bunke, G. Schmieder: “Zum Verhalten von Vanadin in der Umwelt,” *Z. Gesamte Hyg. Ihre Grenzgeb.* **30** (1984).
70. Environmental Health Criteria 81: *Vanadium*, World Health Organization, Geneva 1988.
71. F. H. Nielsen, “Studies on the Essentiality of Some Elements Ascribed as Toxic – Arsenic, Boron, Lead, Tin and Vanadium,” U.S. Department of Agriculture, Agricultural Research Service, Grand Forks Human Nutrition Research Center, Grand Forks, ND.
72. E. J. Underwood: “Vanadium” in: *Trace Elements in Human and Animal Nutrition*, 4th ed., Academic Press, New York 1977, pp. 388–397.
73. R. Nechay: “Mechanism of Action of Vanadate,” *Ann. Rev. Pharmacol. Toxicol.* **24** (1984) 501–524.
74. Natl. Res. Council, Committee on Biolog. Effects of Atmospheric Pollutants, “Vanadium,” National Academy of Science, Washington, D.C., 1977, pp. 117–104.
75. E. P. Levine, *Science (Washington, D.C.)* **133** (1961) 1352.
76. A. R. Byrne, L. Kosta: “Vanadium in Foods and in Human Body Fluids and Tissues,” *Sci. Total Environ.* **10** (1978) 17–30.
77. H. A. Schroeder, J. J. Balassa, I. H. Tipton: “Abnormal Trace Metals in Man: Vanadium,” *J. Chron. Dis.* **16** (1963) 1047–1071.
78. J. Leuschner, H. Haschke, G. Sturm: “New Investigations on Acute Toxicities of Vanadium Oxides,” *Monatsh. Chem.* **125** (1994) 623–646.
79. H. Wienand, W. Ostertag: “Bismutvanadat/molybdat – ein neuartiges Farbpigment,” *Farbe Lacke* **9** (1986) 118 ff.
80. Final Report Vanadium Pentoxide Investigation, Institute for Social Medicine, Innsbruck 1993/94, unpublished.
81. C. Zenz, B. A. Berg, *Arch. Environ. Health* **14** (1967) 709.

Vanillin → **Flavors and Fragrances**

Vapor Deposition → **Thin Films**

Varnishes → **Paints and Coatings**

Vasodilators → **Antihypertensives**

Vat Dyes → **Anthraquinone Dyes and Intermediates**

Veneer → **Wood**

Vermiculite → **Silicates**